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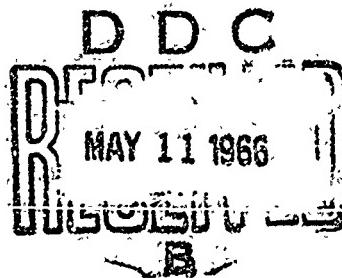
AFAPL-TR-66-35

LITHIUM-ANODE
LIMITED CYCLE BATTERY INVESTIGATION

H. F. Bauman
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LOCKHEED MISSILES & SPACE COMPANY

TECHNICAL REPORT AFAPL-TR-66-35
APRIL 1966



AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

FOREWORD

This is the Annual Report by the Electrochemistry Group, Material Sciences Laboratory, Lockheed Missiles & Space Company, Palo Alto, Calif. under Air Force Contract AF 33(615)-2455, Task 917304 entitled "Lithium-Anode Limited Cycle Battery Investigation." This work was administered under the direction of the Energy Conversion Branch, Aerospace Power Division, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio. The assistance of Mr. Wayne S. Bishop, Task Engineer for the Aero Propulsion Laboratory is acknowledged. The report covers the period February 1965 through December 1965. This report was submitted by the authors 5 March 1966.

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ABSTRACT

This program, to develop the technology necessary to build batteries based on the lithium-cupric fluoride and lithium-cobaltic fluoride couples, was concerned with the development of components as well as battery design.

Propylene carbonate and butyrolactone were the most stable solvents studied and the majority of effort was with these solvents. Conductivities of greater than $10^{-2} \Omega^{-1} \text{cm}^{-1}$ were measured with solutions of NH_4PF_6 in propylene carbonate and several fluorine complex salts in butyrolactone. The influence of water was minimized in these and compatibility tests by direct distillation of solvent into the salt. Solutions of NaPF_6 in propylene carbonate had reasonable stability and were moderately successful as electrolyte for cell tests. Solutions of LiClO_4 in propylene carbonate gave by far the best discharges.

Lithium anodes were prepared from lithium strip and dispersions and gave similar results on cell test. The selection of either type for use in batteries will depend upon fabrication simplicity.

Resistance, electrolyte absorption, and retention were measured for selected separator material. Absorption was generally low for materials compatible with these cell systems.

Sustained cell discharges with a voltage plateau were not obtained with Li-CoF_3 cells even at current densities of 0.5 mA/in.^2 . There was evidence that the cell reaction was that of the Li-CoF_2 couple with a reaction $2 \text{CoF}_3 + \text{Co} \rightarrow 2 \text{CoF}_2$ proceeding chemically.

Discharges of 100 hr above 3.0 V were obtained with Li-CuF₂ cells. The best cell had 58% utilization of CuF₂ with a cell voltage above 3.0 V and delivered 60 W-hr/lb of cell weight. About one-third of the cell weight was electrolyte and improved figures would be expected with larger cells where the electrolyte would be a smaller proportion of the cell weight.

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Section I INTRODUCTION

This is an annual report covering the first 11 months of work, from 1 February 1965 to 1 January 1966, on the lithium-cupric fluoride and lithium-cobaltic fluoride electrochemical couples. These couples are of interest because of their high theoretical energy to weight ratio (746 and 970 W-hr/lb respectively). The development of batteries based on these couples is of particular importance for space vehicle power supplies, where a premium is placed on light weight.

Previous work under Contract AF 33(657)-11709 was concerned with the basic development of these systems. The present 2-year contract will carry the development forward to culminate in the design, fabrication, and test of 1,500 A-h batteries developing 300 W-hr/lb as a goal.

This report is on the portion of the contract which includes the investigation of separator materials and electrolytes, the fabrication of anode and cathode structures, and the design of a 25 A-h battery. The 25 A-h battery is an intermediate goal to evaluate construction and assembly techniques in anticipation of the larger 1,500 A-h battery.

Section II

2.1 ELECTROLYTE STUDIES

The electrolyte is a critical component in a primary electrochemical cell; its physical characteristics affect the operating range of the cell, its resistance contributes to the impedance of the cell, and its stability in contact with the active cell elements has a major effect on the wet storage life of the cell. Solvents with a wide liquid range were selected for this study, and the solubility of various salts and the conductivity of these solutions were determined. Selected solutions were tested for compatibility with other cell components, and comparative cell tests were made with several electrolytes.

2.1.1 Conductivity of Electrolyte Solutions

Measurement of specific conductivity of nonaqueous electrolyte solutions consisting of organic solvents and inorganic salts was initiated. Solutions of the following solvents and coordination salts were prepared in the anhydrous condition and tested at two or more temperatures:

- (a) Dimethyl sulfoxide
Liquid range 18 to 189°C

$$\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{S}}} - \text{CH}_3$$

(b) Propylene carbonate
Liquid range -49 to 241°C

$$\text{CH}_3 - \underset{\text{O}}{\underset{\text{C}}{\text{CH}}} - \text{CH}_2$$

$$\text{O} \quad \text{O}$$

(c) Propylene carbonate - ethylene carbonate mixture (2:1 by volume)
Liquid range 36 to 248°C
(b) plus

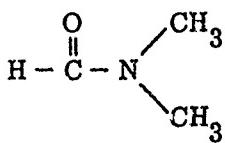
$$\text{CH}_2 - \underset{\text{O}}{\underset{\text{C}}{\text{CH}}} - \text{CH}_2$$

$$\text{O} \quad \text{O}$$

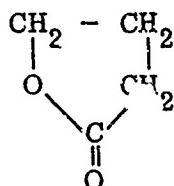
(d) Formamide
Liquid range 2.6 to 210°C

$$\text{H} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{NH}_2$$

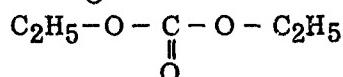
(e) Dimethyl formamide
Liquid range -61 to 153° C



(f) Butyrolactone
Liquid range -43 to 204° C



(g) Diethyl carbonate
Liquid range -43 to 125° C



(h) Propylene carbonate - diethyl carbonate mixture (2:1 molar)
(b) plus (g)

Coordination Salts*

Tetramethyl ammonium hexafluorophosphate	(CH ₃) ₄ NPF ₆
Ammonium hexafluorophosphate	NH ₄ PF ₆
Potassium hexafluorophosphate	KPF ₆
Sodium hexafluoroantimonate	NaSbF ₆
Phenyl trimethyl ammonium hexafluorophosphate	φ(CH ₃) ₃ NPF ₆
Tetramethyl ammonium tetrafluoroborate	(CH ₃) ₄ NBF ₄

In addition, preliminary tests were performed on solutions of propylene carbonate with each of the following salts:*

Ammonium thiocyanate	NH ₄ CNS
Potassium thiocyanate	KCNS
Sodium acetate	NaOOCCH ₃
Ammonium acetate	NH ₄ OOCCH ₃
Sodium perchlorate	NaClO ₄

Each solvent was dried over activated molecular sieve beds (Linde 4AxW) and subsequently vacuum distilled ($P \leq 0.2$ mm) as noted to remove residual water. Salts (except as noted) were dried in a vacuum desiccator containing Drierite at a pressure of ~ 0.5 mm for 24 to 48 hr. Saturated solutions of each of the above salts and each of the dried solvents were prepared in a glove box under argon atmosphere by adding 5-gm increments of the salt to the solvent until no more solute appeared to dissolve at room temperature. Solutions were continually agitated for 8 to 24 hr to ensure saturation, and excess salt was allowed to precipitate by allowing to stand overnight. The approximate degree of solubility was noted.

The water contents of the previously dried and/or distilled solvents, as well as the prepared solutions, were measured by means of the standard Karl-Fischer potentiometric titration technique (iodometric).

*Dried 48 hr in a vacuum oven at ~ 0.5 mm and 110° C and stored in a vacuum desiccator until ready for use.

Care was exercised in the storage and handling of distilled solvents, dried salts, and prepared solutions to minimize contamination and exposure to the atmosphere (and consequent water uptake), particularly before making conductivity measurements. Cleaned and baked glassware was used in all cases.

Specific conductivities of solvents and salt-solvent solutions were measured at each of two or more temperatures (in the range of expected battery service) using a Jones & Bollinger Conductivity Cell of known and periodically remeasured cell constant, and an Impedance Bridge (General Radio Type 1650-A).

The effect of solute concentration on achieving maximum specific conductivity of electrolytes was determined on selected saturated solutions of high conductivity by adding various ratios of each dried solvent to the corresponding prepared solutions and measuring the conductivity. Dilution ratios ranged from 9:1 (solution:solvent) to 1.6:1.

Table I summarizes the data obtained during this period on specific conductivity of electrolytic solvents and solutions at two or more temperatures and, in some cases, various salt concentrations. Included in Table I are the results of water analysis of solvents and solutions, as well as approximate maximum salt concentration limits for the electrolytes.

Results indicate that the following saturated solutions have specific conductivities of about $10^{-2}\Omega^{-1}\text{cm}^{-1}$ or greater:

<u>Saturated Solution</u>	<u>Specific Conductance</u>
DMF + NH_4PF_6	$3.36 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
DMF + NaPF_6	$2.43 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
Butyrolactone + NH_4PF_6	$1.94 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
Butyrolactone + NaPF_6	$1.33 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
DEC + PC + NH_4PF_6	$1.04 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
EC + PC + NH_4PF_6	$1.08 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 23.2°C
PC + NaSbF_6	$1.00 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 23.2°C
PC + NH_4PF_6	$9.68 \times 10^{-3}\Omega^{-1}\text{cm}^{-1}$ at 23.2°C
DMSO + $\phi(\text{CH}_3)_3\text{NPF}_6$	$1.05 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 27.2°C
DMSO + KPF_6	$1.14 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 23.2°C
DMSO + NH_4PF_6	$1.17 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 23.2°C
Formamide + NH_4PF_6	$3.03 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 26.0°C
Formamide + KPF_6	$1.33 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 26.0°C
Formamide + NaSbF_6	$1.00 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 26.0°C

Table I
CONDUCTIVITY OF SALT SOLUTIONS IN VARIOUS SOLVENTS

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Dimethyl Sulfoxide (dist)	$(\text{CH}_3)_4\text{NPF}_6$	Sat. (<20%)	96	Freezes	3.44×10^{-7}	4.55×10^{-7}	
Dimethyl Sulfoxide (dist)	NH_4PF_6	Sat. (<50%)	856	Freezes	7.92×10^{-3}	9.27×10^{-3}	8.94×10^{-3}
Dimethyl Sulfoxide (dist)	NH_4PF_6	Dil. 50% (<25%) (1.5 Molar)	484	7.70×10^{-3}	1.17×10^{-2}	1.66×10^{-2}	1.52×10^{-2}
Dimethyl Sulfoxide (dist)	KPF_6	Sat. (<20%)	2050	9.85×10^{-3}	1.37×10^{-2}	1.62×10^{-2}	1.58×10^{-2}
Dimethyl Sulfoxide (dist)	NaSbF_6	Sat. (<30%)	530	7.92×10^{-3}	1.14×10^{-2}	1.34×10^{-2}	1.34×10^{-2}
Dimethyl Sulfoxide (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. (<50%)	480	7.20×10^{-3}	9.78×10^{-3}	1.28×10^{-2}	
Dimethyl Sulfoxide (dist)	$(\text{CH}_3)_4\text{NBF}_4$	Sat. (<20%)	520	6.86×10^{-3}	1.05×10^{-2} (27.2°C)	7.20×10^{-3} (27.2°C)	
					Freezes		
Propylene Carbonate (dist)	$(\text{CH}_3)_4\text{NPF}_6$	Sat. (<30%)	212	1.80×10^{-6}	2.45×10^{-6}		
Propylene Carbonate (dist)	NH_4PF_6	Sat. (<50%)	424	2.01×10^{-3}	2.52×10^{-3}	2.97×10^{-3}	
Propylene Carbonate (dist)	KPF_6	Sat. (<30%)	406	6.84×10^{-3}	9.68×10^{-3}	1.22×10^{-2}	
					5.04 $\times 10^{-3}$	6.85×10^{-3}	8.30×10^{-3}
							8.33×10^{-3}

Table I (Cont.)

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Propylene Carbonate (dist)	NaSbF ₆	Sat. (< 50%)	776	7.05×10 ⁻³	1.00×10 ⁻²	1.26×10 ⁻²	
Propylene Carbonate (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. (< 50%)	380	5.04×10 ⁻³	8.05×10^{-3} (27.2°C)		
Propylene Carbonate (dist)	$(\text{CH}_3)_4\text{NBF}_4$	Sat. (< 20%)	445	1.68×10 ⁻³	2.39×10^{-3} (27.2°C)		
Propylene Carbonate Ethylene Carbonate 2:1			170	1.23×10 ⁻³	1.59×10^{-5}		
Propylene Carbonate Ethylene Carbonate 2:1	$(\text{CH}_3)_4\text{NPF}_6$	Sat. (< 20%)	254	2.56×10 ⁻³	3.24×10^{-3}	3.86×10^{-3}	
Propylene Carbonate Ethylene Carbonate 2:1	NH ₄ Pf ₆	Sat. (< 40%)	390	7.91×10 ⁻³	1.08×10^{-2}	1.37×10^{-2}	
Propylene Carbonate Ethylene Carbonate 2:1	KPF ₆	Sat. (< 40%)	322	6.00×10 ⁻³	7.91×10^{-3}	9.65×10^{-3}	
Propylene Carbonate Ethylene Carbonate 2:1	NaSbF ₆	Sat. (< 40%)	373	5.00×10 ⁻³	7.05×10^{-3}	8.80×10^{-3}	
Propylene Carbonate Ethylene Carbonate 2:1	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. (< 50%)	312	6.00×10 ⁻³	8.98×10^{-3} (27.2°C)		
Propylene Carbonate Ethylene Carbonate 2:1	$(\text{CH}_3)_4\text{NBF}_4$	Sat. (< 20%)	408	2.66×10 ⁻³	3.54×10^{-3} (27.2°C)		

Table I (Cont.)

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Diethyl Carbonate (dist)	$(\text{CH}_3)_4\text{NPF}_6$	Sat. (< 20%)	420			3.1×10^{-8}	
Diethyl Carbonate (dist)	NH_4PF_6	Sat. (< 20%)	504			$<1.0 \times 10^{-7}$	
Diethyl Carbonate (dist)	KPF_6	Sat. (< 20%)	884			$<1.0 \times 10^{-7}$	
Diethyl Carbonate (dist)	NaSbF_6	Sat. (< 20%)	714			$<1.0 \times 10^{-7}$	
Diethyl Carbonate (dist)			968			2.17×10^{-5}	2.20×10^{-5}
Propylene Carbonate Diethyl Carbonate (2:1 molar)			410			1.32×10^{-6}	1.62×10^{-6}
Propylene Carbonate Diethyl Carbonate (2:1 molar)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. (< 40%)	330			5.32×10^{-3}	7.84×10^{-3} (27.2°C)
Propylene Carbonate Diethyl Carbonate (2:1 molar)	$(\text{CH}_3)_4\text{NBF}_4$	Sat. (< 20%)	355			7.85×10^{-4}	1.07×10^{-3} (27.2°C)
Propylene Carbonate Diethyl Carbonate (2:1 molar)	NH_4PF_6	Sat. (< 20%)	375			7.55×10^{-3}	1.04×10^{-2} (27.2°C)
Formamide (dist)						7.50×10^{-4}	1.05×10^{-3}
Formamide (dist)	$(\text{CH}_3)_4\text{NPF}_6$	Sat. (< 10%)	320			1.38×10^{-3}	1.95×10^{-3} (26.0°C)
			385				

Table I (Cont.)

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Formamide (dist)	NH_4PF_6	Sat. (< 50%)	415	2.01×10^{-2} (26.0°C)	3.03×10^{-2} (26.0°C)	3.03×10^{-2} (26.0°C)	3.03×10^{-2} (26.0°C)
Formamide (dist)	KPF_6	Sat. (< 20%)	485	8.45×10^{-3} (26.0°C)	1.33×10^{-2} (26.0°C)	1.33×10^{-2} (26.0°C)	1.33×10^{-2} (26.0°C)
Formamide (dist)	NaSbF_6	Sat. (< 20%)	430	6.80×10^{-3} (26.0°C)	1.00×10^{-2} (26.0°C)	1.00×10^{-2} (26.0°C)	1.00×10^{-2} (26.0°C)
Dimethyl Formamide (dried)	NH_4PF_6	Sat. (< 20%)	560	2.61×10^{-2} (27.2°C)	3.36×10^{-2} (27.2°C)	3.36×10^{-2} (27.2°C)	3.36×10^{-2} (27.2°C)
Dimethyl Formamide (dried)	NaPF_6	Sat. (< 20%)	580	1.84×10^{-2} (27.2°C)	2.43×10^{-2} (27.2°C)	2.43×10^{-2} (27.2°C)	2.43×10^{-2} (27.2°C)
Butyrolactone (dried)	NH_4PF_6	Sat. (< 20%)	617	1.57×10^{-2} (27.2°C)	1.94×10^{-2} (27.2°C)	1.94×10^{-2} (27.2°C)	1.94×10^{-2} (27.2°C)
Butyrolactone (dried)	NaPF_6	Sat. (< 20%)	520	9.85×10^{-3} (27.2°C)	1.33×10^{-2} (27.2°C)	1.33×10^{-2} (27.2°C)	1.33×10^{-2} (27.2°C)
Propylene Carbonate (dist)	NH_4CNS	Sat. (< 10%)			5.13×10^{-3} (27.2°C)	5.13×10^{-3} (27.2°C)	5.13×10^{-3} (27.2°C)
Propylene Carbonate (dist)	NaOCCCH_3	Sat. (< 10%)			7.94×10^{-6} (27.2°C)	7.94×10^{-6} (27.2°C)	7.94×10^{-6} (27.2°C)
Propylene Carbonate (dist)	$\text{NH}_4\text{OOCCH}_3$	Sat. (< 10%)			1.36×10^{-5} (27.2°C)	1.36×10^{-5} (27.2°C)	1.36×10^{-5} (27.2°C)
Propylene Carbonate (dist)	NaClO_4	Sat. (< 10%)			5.43×10^{-3} (27.2°C)	5.43×10^{-3} (27.2°C)	5.43×10^{-3} (27.2°C)
Propylene Carbonate (dist)	KCNS	Sat. (< 10%)			6.87×10^{-3} (27.2°C)	6.87×10^{-3} (27.2°C)	6.87×10^{-3} (27.2°C)

Table I (Cont.,)

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Dimethyl Formamide (dried)	NH_4PF_6	Sat. sol'n diluted 1:9 with DMF (<2%)				7.19×10^{-3} (27.2°C)	
Dimethyl Formamide (dried)	NH_4PF_6	Sat. sol'n diluted 9:1 with DMF (<18%)				2.11×10^{-2} (27.2°C)	
Dimethyl Sulfoxide (dist)	NH_4PF_6	Sat. sol'n diluted 1:9 with DMSO (<5%)				4.62×10^{-3} (27.2°C)	
Dimethyl Sulfoxide (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 9:1 with DMSO (<45%)				1.09×10^{-2} (27.2°C)	
Dimethyl Sulfoxide (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 4.5:1 with DMSO (<41%)				1.14×10^{-2} (27.2°C)	
Dimethyl Sulfoxide (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 3:1 with DMSO (37.5%)				1.14×10^{-2} (27.2°C)	
Dimethyl Sulfoxide (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 1.6:1 with DMSO (<30.8%)				1.06×10^{-2} (27.2°C)	
Propylene Carbonate (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 9:1 with P. C. (<45%)				8.15×10^{-3} (27.2°C)	
Propylene Carbonate (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 4.5:1 with P. C. (<41%)				8.15×10^{-3} (27.2°C)	
Propylene Carbonate (dist)	$\phi(\text{CH}_3)_3\text{NPF}_6$	Sat. sol'n diluted 2.5:1 with P. C. (<35.7%)				7.42×10^{-3} (27.2°C)	
Butyrolactone	NH_4PF_6	Sat. sol'n diluted 9:1 with B. L. (<18%)				1.85×10^{-2} (27.2°C)	

Table I (Cont.)

Solvent	Salt	Concentration	Water Content (ppm)	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)			
				-12°C	-7°C	23.2°C	32.7°C
Butyrolactone	$\phi(\text{CH}_3)_3\text{NPF}_6$	15				8.4×10^{-3} (24.0°C)	
Propylene Carbonate	LiClO_4	15				4.03×10^{-3} (25.4°C)	
Propylene Carbonate	$(\text{C}_2\text{H}_5)_4\text{NPF}_6$	20				9.98×10^{-3} (25.4°C)	
Propylene Carbonate	$(\text{C}_2\text{H}_5)_4\text{NPF}_6$	20				7.05×10^{-3} (25.4°C)	
Methyl Formate	LiClO_4	60	312.			2.39×10^{-2} (24.0°C)	

From these observations, it is concluded that the most promising salts from the standpoint of solubility and related increase in conductivity of the pure solvent are NH_4PF_6 , NaPF_6 (or KPF_6), NaSbF_6 , and $\phi(\text{CH}_3)_3\text{NPF}_6$, in the order listed. Best solvent conductivity was noted for the propylene/carbonate-ethylene carbonate mixture (2:1 by vol), with a value of $1.59 \times 10^{-5}\Omega^{-1}\text{cm}^{-1}$. However, the addition of salts to this mixture did not increase conductivity as much, relatively, as in other cases (e.g., DMSO).

Studies on the effect of salt concentration of electrolyte conductivity (made by using saturated solutions with additional solvent) showed that slightly dilute solutions (9:1) (e.g., PC + $\phi(\text{CH}_3)_3\text{NPF}_6$) had significantly greater conductivity than saturated solutions. In two cases, DMSO + $\phi(\text{CH}_3)_3\text{NPF}_6$ and DMSO + NH_4PF_6 , reducing the salt concentration by one-half improved the specific conductivity significantly [e.g., for DMSO + NH_4PF_6 from $1.17 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ (sat.) to $1.37 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$ at 1:1 dilution].

Results also indicate that the water content of the solutions was rather high, ranging from 250 to 2,050 ppm (an average of 450 ppm). The chief source appears to be the absorbed and adsorbed moisture in the salts. Improved methods for drying the salts and effecting transfer to the solvents without atmospheric contact have been devised. Laboratory equipment has been designed that will permit vacuum distillation of the solvent and direct transfer to preweighed and predried salts for solution makeup. The results will be discussed in subsection 2.1.2.

2.1.2 Conductivity Measurements in Salt Solutions With Minimum Water Content

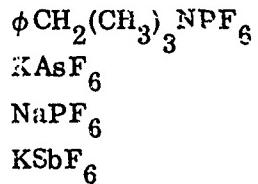
Solutions of propylene carbonate with the following salts were prepared for conductivity and compatibility studies:

Potassium hexafluorostannate	K_2SnF_6
Lithium hexafluorophosphate	LiPF_6
Potassium hexafluoroarsenate	KAsF_6
Potassium hexafluoroantimonate	KSbF_6
Potassium hexafluorophosphate*	KPF_6
Benzyl trimethyl ammonium hexafluorophosphate*	$\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$
Ammonium hexafluorophosphate*	NH_4PF_6
Sodium hexafluorophosphate*	NaPF_6

*These solutions were prepared and tested for conductivity and compatibility previously, as reported in subsection 2.1.1. They were prepared for additional tests using the present techniques to obtain more reliable data based on their lower water content.

Solutions were prepared by direct transfer of freshly distilled solvent to the predried salts to minimize water content according to the following procedure. Salts were dried in a vacuum-desiccator over fresh P_2O_5 for a minimum of 24 hr at a pressure of 0.5 to 1 mm Hg. Accurately weighed quantities (15 to 20 gm) of each salt were then transferred to individual 100-ml round bottom flasks. Four such flasks containing predried salts were attached to the stems of a glass "cow" connected to a vacuum distillation receiver. Teflon stopcocks, incorporated between the flasks and the "cow"-stem, permitted valving off the individual flasks from the rest of the receiver system. A glass delivery tube connected to the distillate receiver is turned within the "cow" to transfer the freshly distilled solvent to each of the four flasks. In practice, the entire distillation system, including the flasks, is evacuated with a mechanical roughing pump to a pressure of 0.5 to 1 mm Hg; the salt in the flasks is heated to 100–120°C by means of a hot-air blower-gun for 15 to 30 min (to drive off remaining adsorbed moisture, water of crystallization, etc.); and 75 ml of freshly distilled solvent is transferred to each flask while maintaining vacuum. To ensure that solvent distillate has the lowest possible water content prior to transfer, the conductivity is determined in situ by means of platinum electrodes embedded in the walls of the receiver prior to transfer to the flasks. Distillate having a specific conductivity higher than $5 \times 10^7 \Omega^{-1}cm^{-1}$ is acceptable and is drained via the internal delivery tube into each flask. The stopcocks adjacent to the flasks are then closed, the receivers removed from the system and agitated, and the evacuated contents stored in a glove box under argon atmosphere until ready for use. The same procedure was used to prepare larger batches of electrolyte solutions (e.g., P. C. & $NaPF_6$, P. C. & $LiPF_6$) for cell discharge tests.

Details of the distillation apparatus and receiver are shown in Figure 1. Solutions of γ -butyrolactone with the following salts were prepared using a smaller distillation apparatus but the same transfer procedure:



Prior to vacuum distillation of γ -butyrolactone (bp 77°C at 1 mm Hg), excess moisture was removed by allowing the solutions to stand over an activated molecular sieve (Linde 4Axw) for 24 hr and passing it through a 75-cm column of the same. A plug of glass wool at the bottom of the column was used for filtering the solvent passing through the column. Water content prior to distillation was 77 ppm.

The water content of the solutions was measured by means of the standard Karl-Fischer potentiometric titration technique and is reported in Table II. Results indicated that the solution preparation and transfer techniques reported were successful in reducing water contents appreciably compared with the previously prepared solutions as reported in subsection 2.1.1. The water content averaged from 39 to 160 ppm (or about 20%.

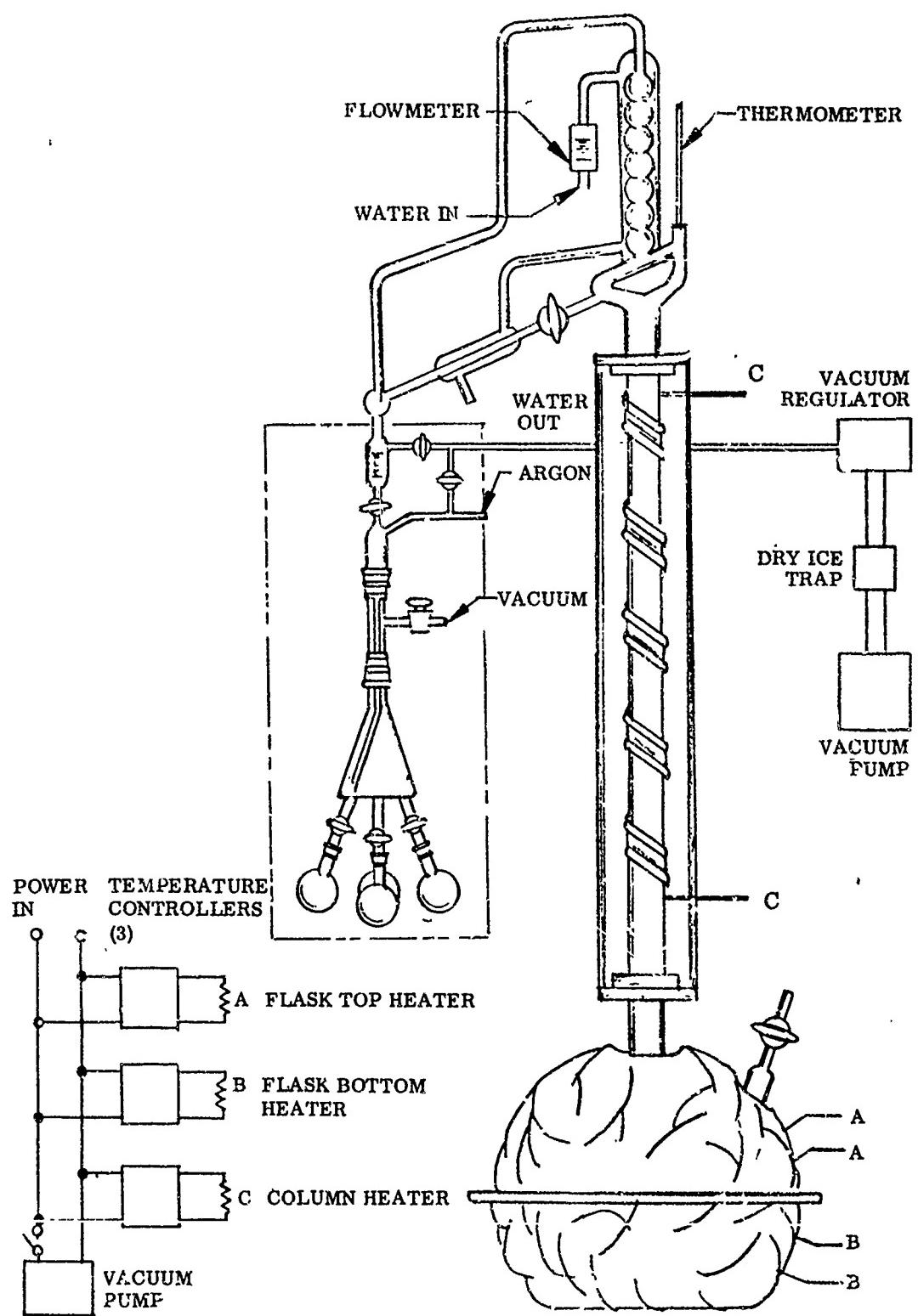


Figure 1 Distillation Apparatus and Receiver Schematic

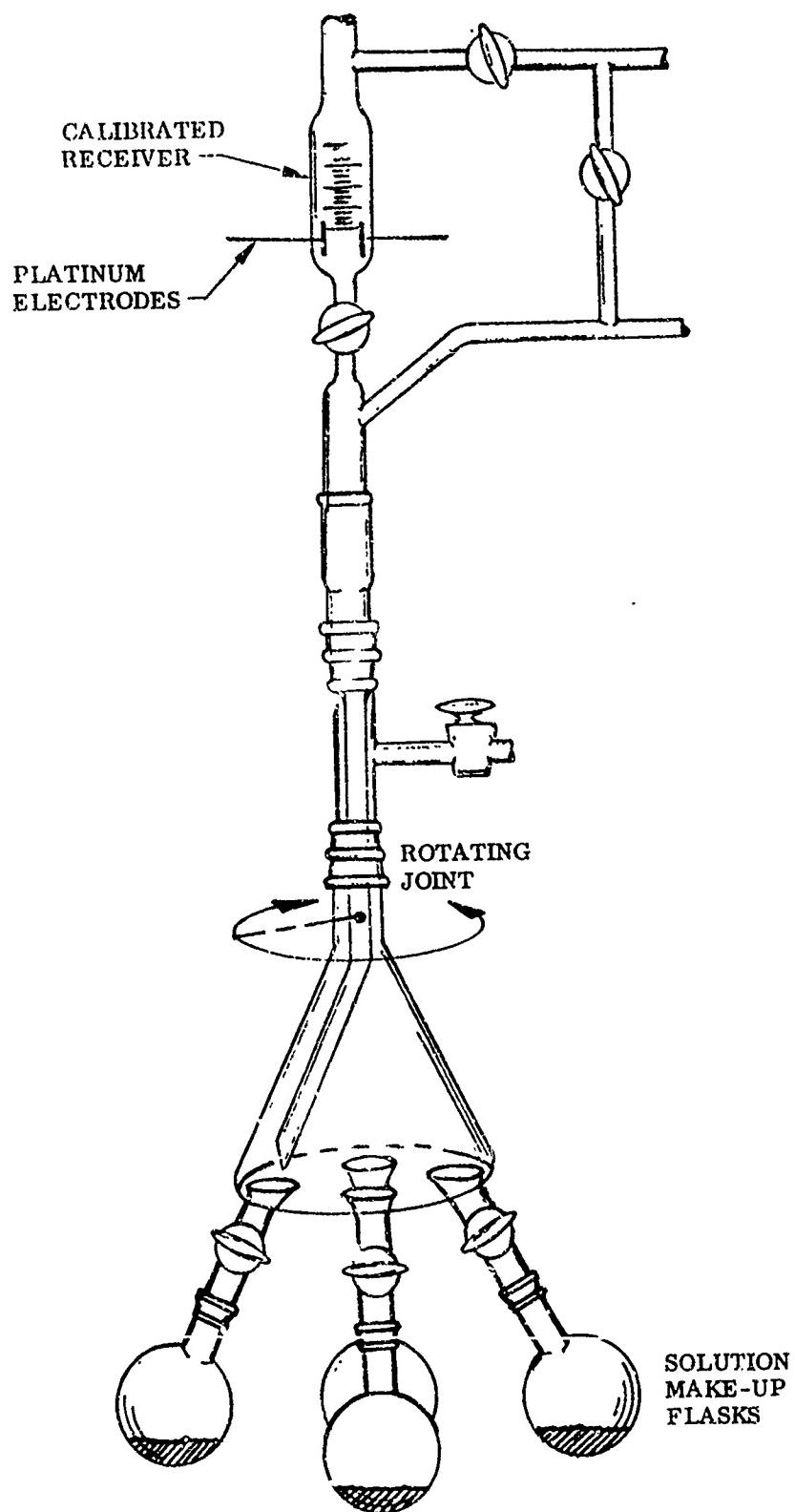


Figure 1 Distillation Apparatus and Receiver Schematic (cont.)

Table II
SPECIFIC CONDUCTIVITY OF SALT SOLUTIONS

Solvent	Salt	Concentration (gm/100 ml solvent)	Specific Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Water Content (ppm)
Propylene Carbonate	K_2SnF_6	< 30	1.28×10^{-4} @ 21.8°C	804
Propylene Carbonate	LiPF_6	< 30	5.65×10^{-3} @ 21.8°C	60
Propylene Carbonate	KAsF_6	< 30	6.88×10^{-3} @ 21.8°C	2590
Propylene Carbonate	KSbF_6	< 30	7.15×10^{-3} @ 21.8°C	120
Propylene Carbonate	KPF_6	30	6.87×10^{-3} @ 23.6°C	40
Propylene Carbonate	KSbF_6 (re-run)	40	7.58×10^{-3} @ 23.6°C	120
Propylene Carbonate	KAsF_6 (re-run)	20	7.95×10^{-3} @ 23.6°C	320
Propylene Carbonate	$\phi\text{CH}_2(\text{CH}_3)_3$ NPF_6	40	7.19×10^{-3} @ 23.6°C	200
Propylene Carbonate	NaPF_6	< 40	6.26×10^{-3} @ 24.2°C	160
Propylene Carbonate	NaSbF_6	< 40	6.85×10^{-3} @ 24.2°C	120
Propylene Carbonate	NH_4PF_6	< 40	1.08×10^{-2} @ 24.2°C	120
Propylene Carbonate	$\phi\text{CH}_2(\text{CH}_3)_3$ NPF_6 (re-run)	< 40	7.39×10^{-3} @ 24.2°C	160
γ -Butyrolactone	$\phi\text{CH}_2(\text{CH}_3)_3$ NPF_6	< 40	1.08×10^{-2} @ 23.2°C	60
γ -Butyrolactone	KAsF_6	< 40	1.38×10^{-2} @ 23.2°C	1430
γ -Butyrolactone	NaPF_6	< 40	1.32×10^{-2} @ 23.2°C	39
γ -Butyrolactone	KSbF_6	< 40	1.16×10^{-2} @ 23.2°C	160
γ -Butyrolactone	K_2SnF_6	< 20	1.32×10^{-2} @ 25.8°C	—

of the values reported for previously made solutions) except in the case of solutions of propylene carbonate and butyrolactone with potassium hexafluoroarsenate, which contained up to 2,590 ppm. It is believed that this salt contained water of hydration which was tenaciously held and not completely removed by the drying procedure followed.

Specific conductivities of salt-saturated electrolyte test solutions were measured at one temperature using a Jones & Bollinger conductivity cell of known cell constant and an Impedance Bridge (General Radio Type 1650-A). Results are presented in Table II. Approximate solubilities of each salt with propylene carbonate and/or γ -butyrolactone are indicated. Results show that conductivities above $10^{-2}\Omega^{-1}\text{cm}^{-1}$ were obtained with all the solutions containing γ -butyrolactone and only one solution containing propylene carbonate (namely, a saturated solution of NH_4PF_6). In general, the conductivities are somewhat lower than those previously determined for similar solutions as reported in subsection 2.1.1. This may be attributed to lower salt solubilities as a result of the more anhydrous nature of the presently prepared solutions.

To obtain additional information on the effect of water on nonaqueous electrolyte solutions, the effect of moisture content on the specific conductivity of saturated solutions of sodium hexafluorophosphate in propylene carbonate was determined as follows:

- Solution 2.1. Based on the original water content (32 ppm) of the saturated solution prepared as described previously, calculated quantities of distilled water were added with micropipettes to three aliquots of this solution (containing excess salt) in order to increase the nominal moisture content to 1,000, 2,000, and 10,000 ppm.
- Solution 2.2. Specific conductivities of these solutions were determined at 25.2° C as previously described. Results are shown in Figure 2.

The concentration versus specific conductivity of sodium hexafluorophosphate-propylene carbonate solutions was determined in accordance with the following procedure:

- Solution 1.1. One liter of saturated solution of NaPF_6 in propylene carbonate was prepared by distilling the solvent directly into a flask containing the preweighed (138 gm) and predried salt under vacuum ($p \sim 1 \text{ mm Hg}$) conditions. The solution was repeatedly agitated and allowed to reach equilibrium over a 24-hr period. Approximately 100 gm of salt dissolved in 1 liter of solvent.
- Solution 1.2. An aliquot of saturated solution was diluted with an equal volume of freshly distilled propylene carbonate.
- Solution 1.3. An aliquot of the dilute solution was diluted again with an equal volume of freshly distilled propylene carbonate. (The dilution ratio of the original saturated solution was 1:4.)

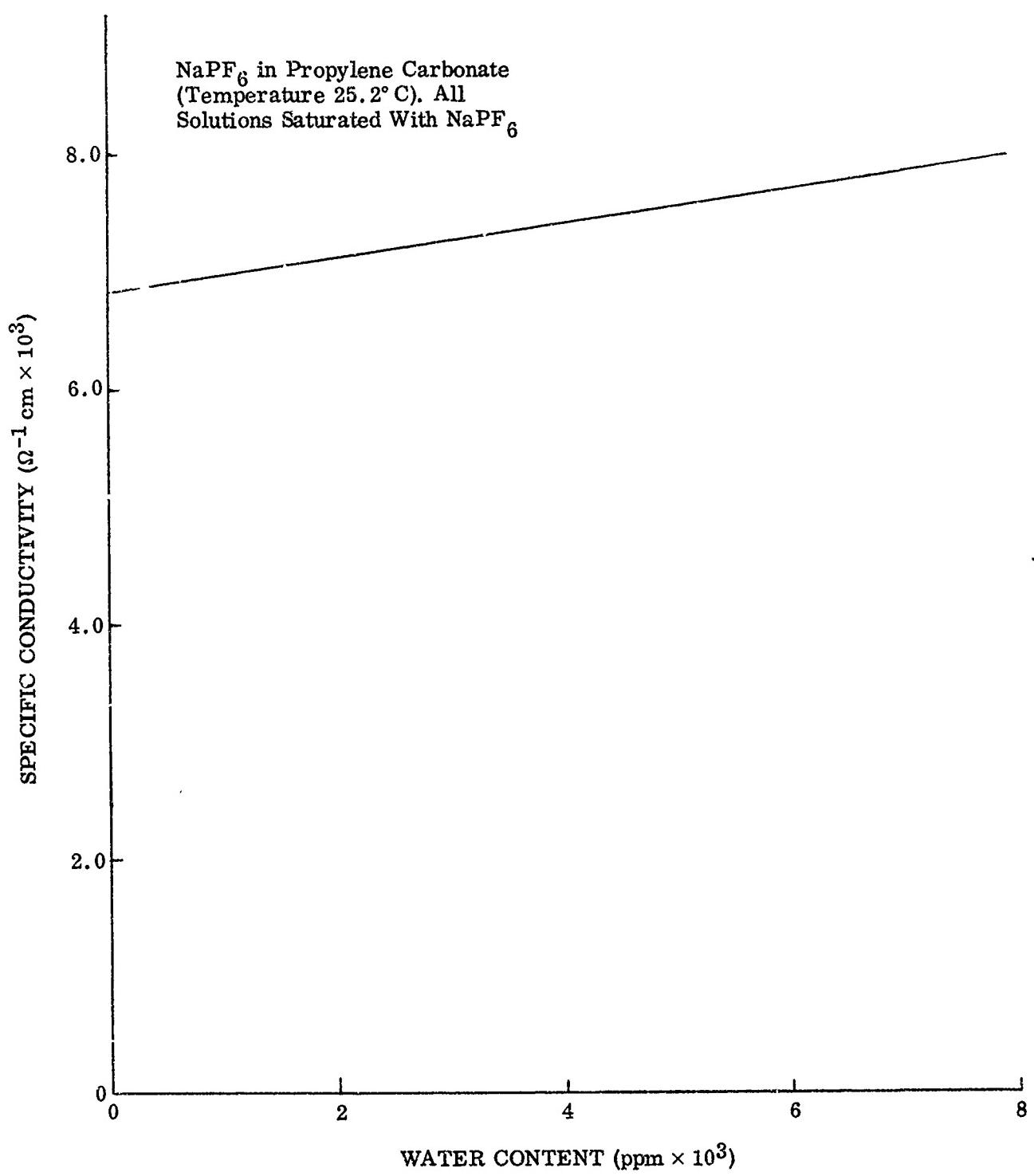


Figure 2 Effect of Water Content on Conductivity of NaPF₆ - Propylene Carbonate Solutions

Solution 1.4. Specific conductivities of the foregoing solutions were measured at 25.3°C with a Jones & Bollinger conductivity cell of known cell constant and an impedance bridge (General Radio Type 1650-A). Results are given in Figure 3.

The equivalent conductance at each of three concentrations of NaPF₆ in propylene carbonate was calculated from the known concentrations and specific conductivities (reported in Table I) and the following relationship:

$$\Lambda = \frac{(1000)L_{(ions)}}{C}$$

where

Λ = equivalent conductance (Ω^{-1})
 L_{ions} = specific conductivity of ions [= $L_{(solution)} - L_{(solvent)}$]
 C = concentration of salt (gm-eq/l)

Equivalent conductance data are reported in Table III.

Table III

EQUIVALENT CONDUCTANCE DEGREE OF DISSOCIATION
AND IONIZATION CONSTANT FOR NaPF₆-PROPYLENE
CARBONATE SOLUTIONS

Solution No.	NaPF ₆ Concentration (moles/liter)	Equivalent Conductance $\Lambda(\Omega^{-1})$ (@ 25.3°C)	Degree of Dissociation (α)	Ionization Constant (K _a)
1.1(sat.)	0.696	9.55	0.34	0.12
1.2	0.348	14.38	0.51	0.19
1.3	0.174	18.85	0.67	0.24

A plot of equivalent conductances versus the square roots of the corresponding concentrations indicated a linear relationship characteristics of strong electrolyte behavior (Kohlrausch's Rule). The value of equivalent conductance at infinite dilution for NaPF₆ in propylene carbonate was readily obtained by extrapolating the line to zero concentration ($\Lambda_0 = 28$) as shown in Figure 4.

This value is within the range reported in the literature ($\Lambda_0 = 28 - 31$)* for some alkali halides (e.g., KI and NaI) in propylene carbonate.

*Harris, W. S., "Electrochemical Studies in Cyclic Esters," University of California (Berkeley) Radiation Laboratory Report UCRL-8381 (Thesis), 17 July 1958.

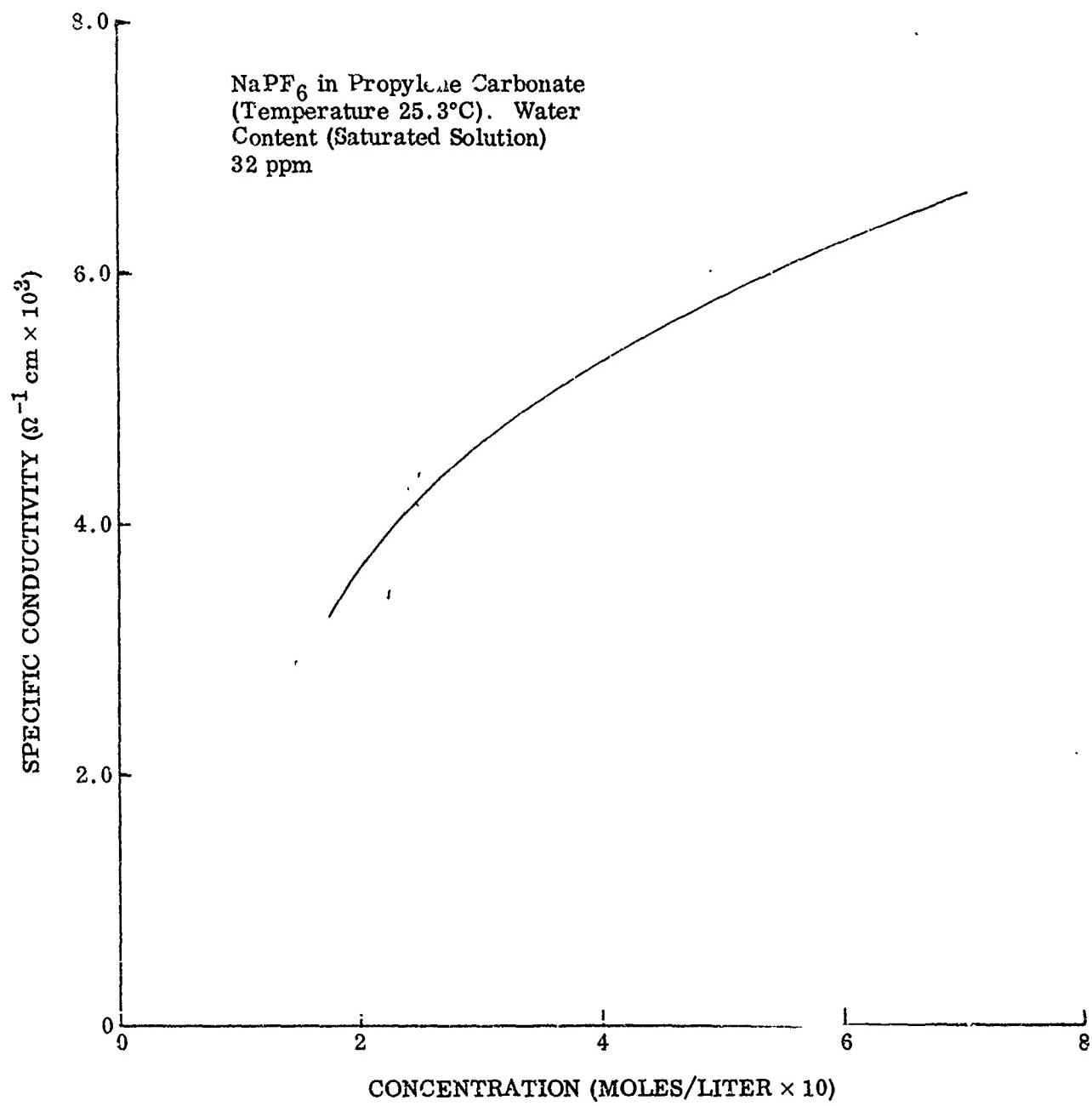


Figure 3 Effect of NaPF₆ Concentration on Conductivity of Propylene Carbonate Solutions

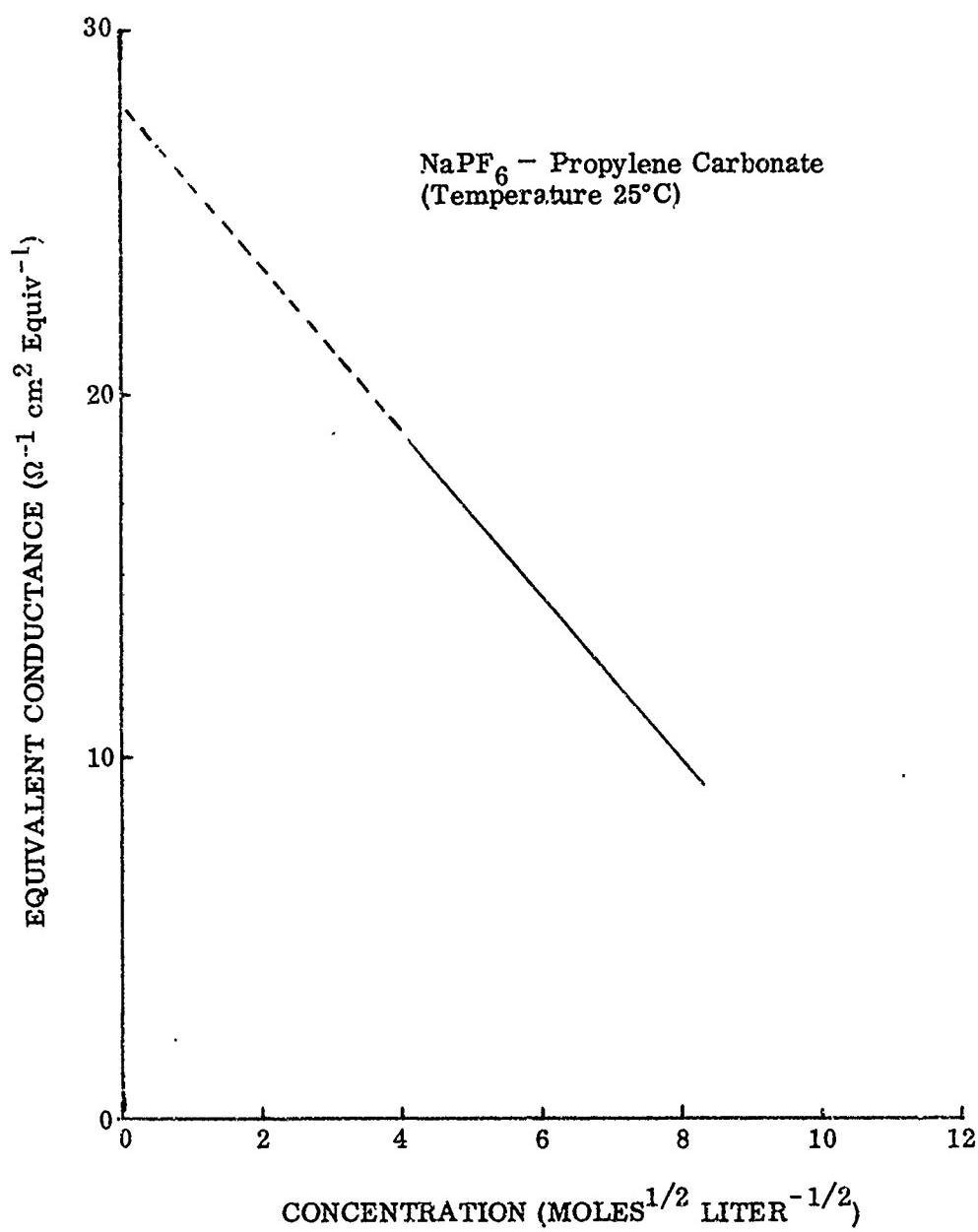


Figure 4 Kohlrausch Plot for NaPF₆ - Propylene Carbonate

It is of interest to calculate the degree of dissociation and the ionization constant of the salt in solution from the derived electrochemical data. These parameters were calculated from the following relationships and are reported in Table III.

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad K_a = \frac{[\text{Na}^+][\text{PF}_6^-]}{[\text{NaPF}_6]} = \frac{\alpha^2 C}{1 - \alpha}$$

2.1.3 Determination of Solubilities of Alkali Fluorides in Propylene Carbonate From Electrochemical Data

In the discharge of the lithium-CuF₂ battery, lithium ions and fluoride ions are generated at the anode and cathode, respectively. In addition, ions from the dissociation of the salt are present in the electrolyte. These ions can interact to produce a precipitate. Thus, in the case of NaPF₆-propylene carbonate electrolyte, Na⁺ and Li⁺ are in competition for PF₆⁻ and F⁻ in solution. The least soluble salt, whether NaF or LiF, will precipitate out of solution. (Alkali halides are very insoluble in cyclic organic esters, leaving Li⁺ and PF₆⁻ or Na⁺ and PF₆⁻, respectively, in solution.)

To determine which species precipitate and which remain in solution, it was necessary to measure the solubilities of selected alkali fluorides of interest in propylene carbonate. Solubilities were calculated from the electrochemical properties of saturated dry solutions of KF, LiF, and NaF in propylene carbonate prepared in a manner similar to that described for Solution 1.1. Results are given in Table IV.

Table IV

SOLUBILITIES OF ALKALI FLUORIDES IN PROPYLENE CARBONATE (Calculated From Conductivity Data)

Solution Composition	Specific Conductivity at 25°C (551 cm ⁻¹)	Assumed Equivalent Conductance at 25°C (Λ)(Ω ⁻¹)	Solubility (Concentration at Saturation) (gm/100 ml)
PC	3.25 × 10 ⁻⁷	—	—
PC+KF(sat.)	1.50 × 10 ⁻⁵	28	2.9 × 10 ⁻³
PC+LiF(sat.)	1.99 × 10 ⁻⁶	28	1.5 × 10 ⁻⁴
PC+NaF(sat.)	7.60 × 10 ⁻⁷	28	6.1 × 10 ⁻⁵

Solubility calculations were made from the measured specific conductivities at 25° C and the assumed values of equivalent conductance reported in the literature* for certain alkali halides (e.g., $\Lambda_0 = 28 - 31$ for KI and NaI). The following relationship was used to calculate the reported values:

$$C = \frac{(1000)L_{(\text{ions})}}{\Lambda_0}$$

where C is the solubility of the salt and assuming that all of the dissolved salt exists in simple ionic form. Results indicate that solubilities decrease in the following order: KF, LiF, and NaF. The solubilities decrease roughly by one order of magnitude for each salt. Hence, it is concluded that in the NaPF_6 -propylene carbonate system, NaF will precipitate out on cell discharge, leaving Li^+PF_6^- as the electrolyte. Conversely, if KPF_6 electrolyte were used, LiF would precipitate and K^+PF_6^- would remain in solution.

2.1.4 Electrolyte Compatibility Studies

The following solutions previously tested for conductivity were individually added in 20-ml aliquots to 1-gm quantities of lithium metal, anhydrous cobalt trifluoride (CoF_3), and anhydrous cupric fluoride (CuF_2) in a glove box under argon atmosphere. Care was exercised not to introduce moisture or contaminants into the test reagents.

DMSO + NaPF_6
Propylene carbonate + NH_4PF_6
DMSO + NaSbF_6
Propylene carbonate + NaSbF_6
Formamide + NH_4PF_6
DMSO + NH_4PF_6
Propylene carbonate + $\phi(\text{CH}_3)_3\text{NPF}_6$
Butyrolactone + NaPF_6
Butyrolactone + NH_4PF_6
Dimethyl formamide + NaPF_6
Dimethyl formamide + NH_4PF_6

The reagents were sealed in screw-lid glass jars equipped with polyethylene film liners and observed for evidence of reaction such as color change, precipitation, gas evolution, etc. The test solutions were stored and observed periodically for evidence of slow reactions. The results, presented in Table V, indicate that the butyrolactone solutions with NaPF_6 and NH_4PF_6 were the most compatible with the test reagents,

*Ibid.

Table V

CHEMICAL COMPATIBILITY OF ELECTROLYTE TEST SOLUTIONS
WITH ANODE AND CATHODE MATERIALS

Electrolyte (Test Solution Sat.)	Compatibility Test Observations					CoF ₃
	Immediate		12-14 Days			
Li	CuF ₂	CoF ₃	Li	CuF ₂		
DMSO+NH ₄ PF ₆	Reacts vigorously-gas evolution sulfide odor, cl. Li edges turn white	Blue-green sol'n	Brown sol'n (possibly no rx)	Dark brown sol'n Li completely reacted	Deep-blue sol'n and precipitate	Brown sol'n
DMSO+NaPF ₆	Reacts-gas evolution Sol'n yellows	Blue-green sol'n	Sol'n cloudy pink	Brown sol'n	Deep blue-green sol'n	Red-violet sol'n
DMSO+NaSbF ₆	Reacts-gas evolution Sol'n yellows precipitation	Blue-green sol'n	Sol'n cloudy pink	Brown sol'n	Deep blue-green sol'n	Red-violet sol'n
PC+NH ₄ PF ₆	Slight reaction-Sol'n cloudy	No effect (sol'n clear)	Sol'n cloudy	White reactant on Li, Sol'n cloudy	Pale-yellow sol'n	Red-violet sol'n
PC+NaSbF ₆	Reaction. Sol'n cloudy & thickens. Li discolored gas evolution	scl'n cloudy brown	Sol'n cloudy brown	Discolored Li and sol'n	Pale-yellow sol'n	Red-violet sol'n
PC+ ϕ (CH ₃) ₃ NPF ₆	Sol'n cloudy	Pale-yellow sol'n (no effect?)	Light brown	Sol'n cloudy, yellow sol'n Li discolored	Pale-yellow sol'n (no effect?)	Red-violet sol'n
Formamide +NH ₄ PF ₆	Violent reaction heat evolved (Li removed)	Deep blue sol'n	Red-violet sol'n	—	Very deep blue sol'n	Deep red-violet sol'n

Table V (Cont.)

Electrolyte (Test Solution Sat.)	Compatibility Test Observations					
	Immediate		12 - 14 Days			
	Li	CuF ₂	CoF ₂	Li	CuF ₂	CoF ₃
DMF+NH ₄ PF ₆	Sol'n slightly cloudy	Sol'n cloudy & light blue	Sol'n cloudy & brown	Li has white deposit. Sol'n clear. White precipitate	Pale-green sol'n	Dark red-brown, cloudy sol'n
DMF+NaF - 6	Clear (no effect)	Sol'n cloudy & milky white ppt.	Sol'n cloudy & brown	Dark brown sol'n amine odor. Li discolored	Blue-green sol'n	Pale red-violet sol'n
Butyrolactone +NH ₄ PF ₆	No effect (sol'n clear)	Blue sol'n	Brown sol'n	Li discolored, reacted	Green-brown sol'n & ppt.	Brown sol'n & ppt.
Butyrolactone +NaPF ₆	Sol'n slightly cloudy	Sol'n slightly cloudy	Sol'n slightly cloudy & brown	White ppt. but Li O.K. & sol'n clear	Deep-blue sol'n	Brown sol'n

although the blue color of the solution with CuF₂ indicates that some complexing may have occurred. All other solutions reacted with lithium. Complexing and/or reduction of Co may have occurred in most cases with the solutions in the presence of CoF₃. It is possible that the traces of water present in the electrolyte test solutions as reported may have influenced the compatibility test results. Steps are being taken, as described previously, to reduce the moisture content and furthermore to effect transfer of solutions to test reagents under vacuum or inert atmosphere to minimize water entrapment. Also, sealed glass ampules will be used in the future for storage and observation of compatibility test solutions, as described in subsection 2.1.5.

2.1.5 Compatibility Studies in Sealed Glass Containers

Electrolyte test solutions, previously tested for conductivity and water content, were individually added in 10-ml aliquots to 1/4-gm quantities of lithium metal and 1/2-gm quantities of anhydrous cobalt trifluoride and anhydrous cupric fluoride in a glove box under argon atmosphere. Solutions were carefully transferred with hypodermic syringes from the original distillation receiver flasks to 20-ml glass ampoules containing the preweighed anode and cathode test materials. The ampoules were tightly corked after transfer to the glove box, removed from the box, and individually tipped with a torch to seal the contents in all glass containers. The test solutions were stored and observed periodically for evidence of reaction (e.g., color changes, precipitation, and gas evolution).

The following test solutions were prepared in the manner described and checked for compatibility with Li, CoF₃, and CuF₂:

Propylene carbonate + KPF₆
Propylene carbonate + KSbF₆
Propylene carbonate + KAsF₆
Propylene carbonate + $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$
Propylene carbonate + NaPF₆
Propylene carbonate + NaSbF₆
Propylene carbonate + NH₄PF₆
 γ -Butyrolactone + $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$
 γ -Butyrolactone + KAsF₆
 γ -Butyrolactone + KSbF₆
 γ -Butyrolactone + NaPF₆

Observations are reported in Tables VI, VII, and VIII. Judging by the color change of the solution or the appearance of the lithium surface, the most stable electrolyte with

Table VI
CHEMICAL COMPATIBILITY OF ELECTROLYTES
WITH LITHIUM

Electrolyte Test Solution (Saturated)	Immediate - 1 Day	12--20 Days Li	6-7 Weeks
PC+KPF ₆	No reaction	No rx; sol'n slightly yellow	Li Bright; sol'n clear amber
PC+KSbF ₆	No reaction but edges of Li appeared dull	Edges of Li blackened and complete sur- face became black; sol'n clear	Li very black; sol'n clear
PC+KAsF ₆	No reaction but edges of Li appeared tar- nished	Li surface be- came very black; sol'n clear	Li very black; sol'n pale yellow
PC+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	Sol'n turbid (white); Li o. k.	Li tarnished; sol'n turbid (white precipitate)
PC+NaPF ₆	No reaction	No rx; sol'n clear; Li o. k.	Li tarnished; sol'n turbid (white precipitate)
PC+NaSbF ₆	No reaction	Sol'n grayish; Li very black	Li very black; sol'n clear
PC+NH ₄ PF ₆	Immediate Rx; fizzing(gas evo- lution); heat evolved	Reacted	
BL+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	Sol'n amber; Li o. k.	Li bright; sol'n amber
BL+KAsF ₆	No reaction but edges of Li tarnished	Li surface blackened; sol'n clear	Li gray-black; sol'n clear
BL+KSbF ₆	No reaction but edges of Li tarnished	Li surface blackened; sol'n amber	Li very black; sol'n clear
BL+NaPF ₆	No reaction	Li o. k.; sol'n amber	Li bright; sol'n yellowish

Table VII
CHEMICAL COMPATIBILITY OF ELECTROLYTES
WITH CUPRIC FLUORIDE

Electrolyte Test Solution (Saturated)	Immediate -1 Day	12-20 Days	6-7 weeks
PC+KPF ₆	No reaction	No rx; sol'n clear	Solution clear
PC+KSbF ₆	No reaction	No rx; solution clear	Solution clear
PC+KAsF ₆	No reaction	No rx; solution clear	Solution clear
PC+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	No rx; sol'n clear	Solution clear
PC+NaPF ₆	No reaction	Sol'n slightly amber but clear	Solution brown-black; white precipitate
PC+NaSbF ₆	No reaction	No rx; solution clear	Solution pale green
PC+NH ₄ PF ₆	No reaction	No rx; solution clear	
BL+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	No rx; solution clear	Solution faint green
BL+KAsF ₆	No reaction	N rx; solution clear	Solution faint green
BL+KSbF ₆	Pale green solution	Solution green	Solution blue-green
BL+NaPF ₆	Pale green solution	Solution greenish-black	Solution brown-black; white precipitate

Table VIII
CHEMICAL COMPATIBILITY OF ELECTROLYTES
WITH COBALTIC FLUORIDE

Electrolyte Test Solution (Saturated)	Immediate - 1 Day	12-20 Days	6-7 weeks
PC+KPF ₆	No reaction	Sol'n slightly amber but clear	Solution clear
PC+KSbF ₆	No reaction	Sol'n slightly amber but	Solution red-brown
PC+KAsF ₆	No reaction	Sol'n slightly pink but clear	Solution dark red-brown
PC+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	Sol'n slightly amber but clear	Solution pale amber
PC+NaPF ₆	No reaction	Sol'n slightly amber but clear	Sol'n magenta; white precipitate
PC+NaSbF ₆	No reaction	Sol'n slightly amber but clear	Sol'n light brown-pink
PC+NH ₄ PF ₆	No reaction	Sol'n slightly amber but clear	
BL+ $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	No reaction	Sol'n dark brown	Solution brown-black
BL+KAsF ₆	No reaction	No rx; sol'n clear	Solution red-brown
BL+KSbF ₆	No reaction	Sol'n dark red-brown	Solution brown-black
BL+NaPF ₆	No reaction	Sol'n dark red-brown	Sol'n dark red- brown; white precipitate

lithium is PC+KPF₆; NaPF₆ or $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$ in either PC or BL show fair compatibility. All the electrolytes tested with CuF₂ appeared to be stable, except that NaPF₆ in either PC or BL was stable for a short time and then darkened.

Solutions of KPF₆ in PC and $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$ in PC showed little reaction with CoF₃. All the BL solutions reacted, indicating that this solvent is somewhat less than PC.

2.2 SEPARATOR STUDIES

The separator is an electrochemical cell serving the dual purpose of keeping the two electrodes separated while simultaneously allowing penetration by the electrolyte so that an ionic conducting path may exist between the electrodes. The mechanical separation between the cells must be sufficient to prevent shorting; the ionic conducting path should have as low a resistance as possible. The resistance of the separator increases with the thickness and decreases as the porosity becomes greater, porosity here being considered to be the area of the separator that allows ionic conduction. In cells where the electrolyte does not directly enter the electrode reactions, the thinnest separator with the maximum porosity will give the lowest resistance and have the lowest power loss during discharge.

The separator resistance was measured in a fixture with flooded separator held between two silver-faced pistons in a polytetrafluoroethylene tube. The dry and wet thicknesses of the separator were also measured in this fixture with the aid of a surface plate and a dial indicator. Because of the large faces and close spacing of the electrodes in the fixture, a capacitive element was introduced into the measurement. The series capacitance C_s and dissipation factor D are measured with an AC bridge. From these data, the resistance per circular inch of the material is calculated by the following formula:

$$R = \frac{D}{2\pi C_s}$$

A sodium hexafluorophosphate solution (0.8 moles/liter) in propylene carbonate was used as the electrolyte in this test. It was prepared from commercial solvent without dehydration and had a resistance of $7 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$.

Two other characteristics of separators are important for cells that are to operate in space vehicles: the absorption of electrolyte by the separator and its retention during acceleration. Sufficient absorption and retention will maintain electrolyte between the electrodes so that normal discharge will continue during the environmental conditions encountered in such applications. The methods for measuring these characteristics are similar to those suggested for separators for alkaline silver oxide-zinc batteries.*

*J. E. Cooper and A. Fleischer, eds., Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries, AF Aero Propulsion Laboratory, n.d.

The absorption is measured by immersing the sample in electrolyte and soaking, wiping off, and weighing. The weight of the absorbed electrolyte (the difference between wet and dry separator weight) divided by the dry separator weight is given as the absorption figure.

The retention was measured by placing the separator sample, supported by a screen, in a fixture (Figure 5) and placing the fixture in a centrifuge. The fixture was rotated at a speed which subjected it to an acceleration 25 times gravity and maintained at that speed for 2 min. The sample was then removed from the fixture and weighed and the retention represented as a percentage of the absorbed electrolyte retained after centrifugation.

The resistance, absorption, and retention measured for a variety of separator materials are given in Table IX. Absorption and retention are similar to those measured with aqueous electrolytes, although the higher absorption values were measured with separators for aqueous electrolytes. The glass fiber felts still appear to have the best combination of favorable characteristics for use in nonaqueous cells.

2.3 LITHIUM ANODE STUDIES

Lithium metal is commercially available as extruded strip and as dispersions, as well as rod and other more massive forms. The form in which lithium is used as an anode will depend upon the polarization and utilization of the lithium and upon the ease with which electrodes can be fabricated at present, the current densities obtainable from Li-CuF₂ allow the use of sheet lithium without excessive polarization. As higher current density cathodes are fabricated, higher current density anodes will be required and higher surface area electrodes may be necessary. Polarization is not only a loss of useful energy but also increases the problems of thermal control of the battery when used in a space vehicle.

The majority of the cells tested on this program used anodes prepared by rolling strip lithium on silver or nickel expanded metal. This method was used because of its simplicity and adaptability to electrodes of different sizes.

A test fixture that allowed the use of reference electrodes with both cell electrodes, Figure 6 was prepared for the evaluation of lithium anodes as well as prepared cathodes. It consisted of a polypropylene block with cavities on both sides to hold electrodes which were connected by a substantial electrolyte chamber. Both shoulders holding the electrodes in place were drilled at 45 deg for Lugin capillaries connecting to reference electrode chambers. This block cell was assembled in the dry box with appropriate electrodes and placed in a commercial Pyrex fitting which was closed by an O-ring gasketed polytetrafluoroethylene plate holding feedthrough electrical connections. This assembly could then be removed from the dry box for test.

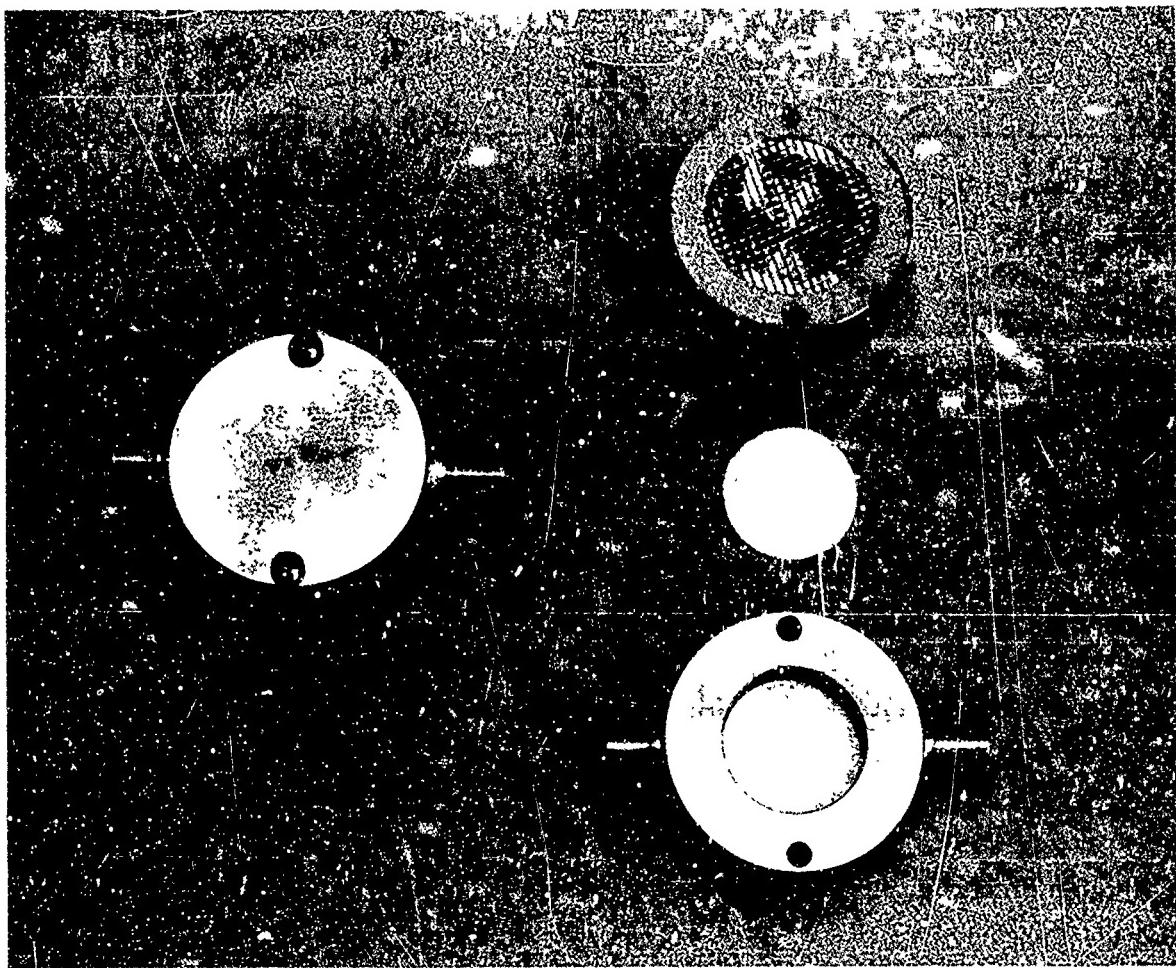


Figure 5 Electrolyte Retention Fixture

Table IX
CHARACTERISTICS OF SEPARATOR MATERIAL

Material	Identifi-cation	Thickness		Resistance (ohm/in. ²)	Absorption	Retention (%)
		Dry (in.)	Wet (in.)			
Membrane Filter	6424	.027	.027	7.3	6.10	100
Membrane Filter	6429	.027	.029	8.8	5.33	80
Glass Fiber Paper	Type G	.040	.039	7.3	6.06	85
Glass Fiber Paper	Type E	.020	.019	3.0	8.70	98
Glass Fiber Paper	Type A	.025	.024	3.8	4.03	95
Glass Fiber Paper	231	.011	.011	2.5	7.43	90
Glass Fiber Paper	221	.003	.003	13.	4.03	54
Glass Fiber Paper	122	.005	.005	3.3	2.22	56
Polyolefin Film, Porous	H1250	.032	.032	6.9	1.03	78
Polyolefin Film, Porous	14PN	.010	.011	1.8	2.09	99
Polycarbonate Film	-	.006	.006	21.5	.093	53
Polycarbonate Film	-	.002	.002	4.1	.140	85
Cellulosic Gauze	478	.006	.006	10.7	1.12	98
Cellulosic Nonwoven	R2201	.005	.004	4.73	10.1	60
Polyester Nonwoven	EM345	.004	.004	7.7	.018	55
Polyester Nonwoven	EM346	.005	.005	17.	.080	54
Polyester Nonwoven	EM343	.004	.004	20.4	.440	95
Polyolefin Nonwoven	SM91	.006	.006	14.4	1.62	94
Polyolefin Nonwoven	EM476	.004	.004	4.4	.993	98
Cellulosic Paper	705-C	.003	.003	3.9	.037	100
Acrylic Paper	922D	.007	.007	6.0	205	99
Acrylic Paper	922B	.010	.010	7.2	.375	99
Cellulosic Film	300	.001	.001	122.	.100	58
Cellulosic Film	600	.001	.001	202.	.183	68

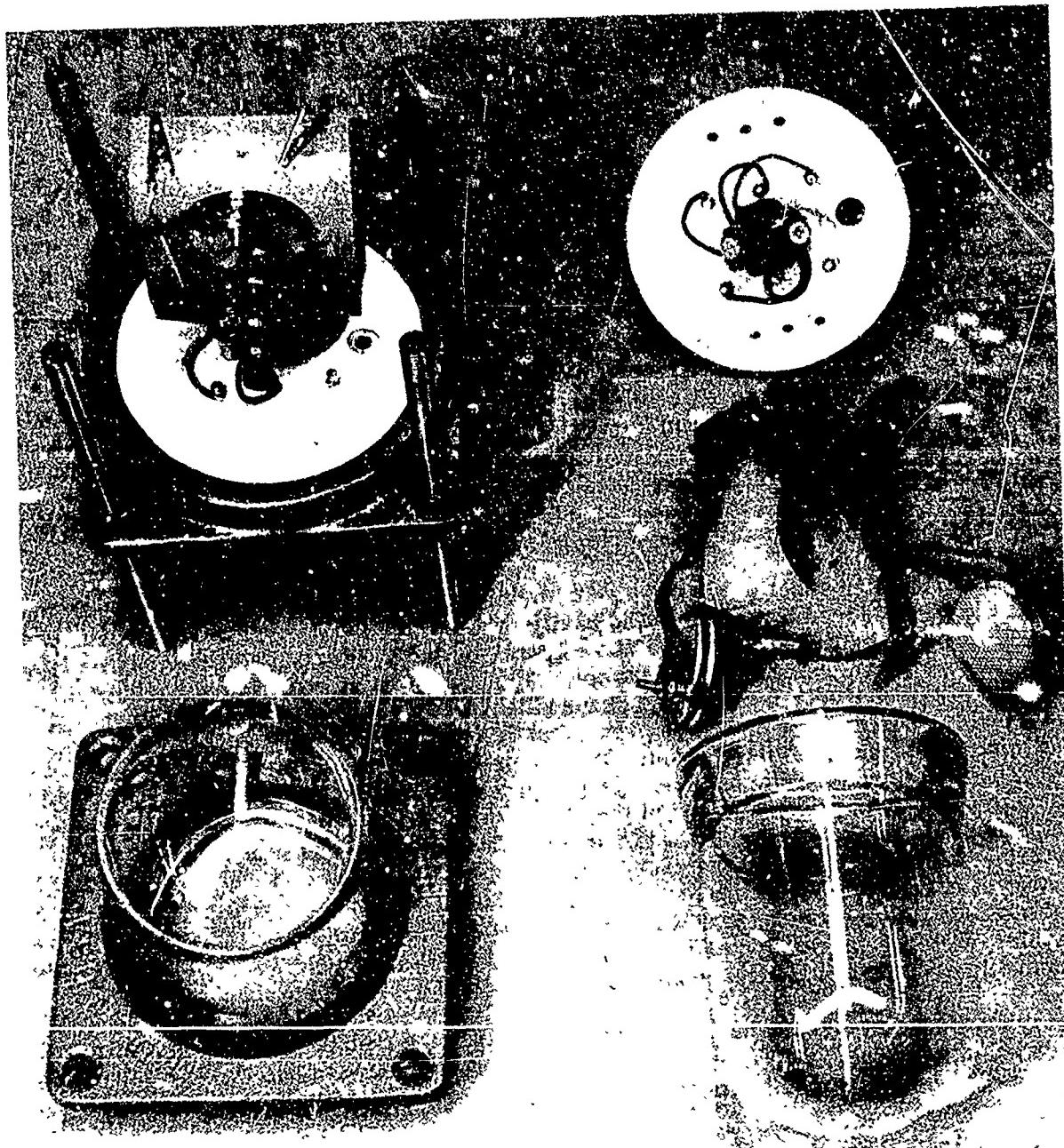


Figure 6 Electrode Test Cell

Lithium wire was used as the reference electrode. Sheet lithium rolled on expanded silver mesh was used for preliminary runs with a PC-NaPF₆ electrolyte. In the first tests, slightly higher polarization values were measured than had previously been recorded.* This could be the result of the film on the lithium caused by higher water content than normal in the assembly dry box, or by water in the electrolyte.

Anodes were prepared from lithium dispersions. A commercially available lithium with 50% solids and 100 μ or less in hydrocarbon solvent was pasted on expanded nickel sheet and pressed at 2T/in.² with the die faces protected with polyester film. Circular electrodes were cut and washed in ethyl ether and propylene carbonate to remove the dispersion solvent. The electrodes were assembled in block cells with side Lugin capillaries connecting to a chamber with a lithium wire reference cell. Two cells were prepared with sheet lithium anodes, and two with lithium dispersion anodes. One cell in each group had a CuF₂-silver flake cathode and one a CuF₂-copper flake cathode. The electrolyte in all cases was IM NaPF₆-propylene carbonate. The initial load on the cells was increased in steps from 1 to 7.2 mA/in.². With both anode types, a high initial polarization occurred as load was applied, with but slight increase with increasing load. Polarization was about 500 mV in all cases at 7.2 mA/in.². When the load was returned to 1 mA/in.², the polarization was about one half the initial value, and during continued discharge it decreased in all cases.

In another effort, a sheet of plastic 0.032 in. thick was cut to encircle a 2-in. by 2-in. electrode and fastened to a plate. The cavity in which the electrode grid was placed was filled with dispersed lithium (50% Li by weight in hydrocarbon solvent, particle size 100 μ or less), using a plastic trowel. A uniform distribution was not achieved because of the characteristics of the suspension, but the assembly was bagged in polyethylene and the electrode was pressed at 30T, 7.5 T/in.² outside the glove box and returned to the box for removal. The bottom of the fixture was protected from the lithium with adsorbent paper and the punch face with polytetrafluoroethylene film during the pressing. The surface of the electrode was smooth after pressing and was brightly metallic, but the grid was distorted. The electrode was trimmed to 2-in. by 2-in. and assembled in a bag-type cell. Its operation in the cell was very similar to that of sheet lithium electrodes. Although actual polarization measurements were not taken on this electrode, it appears that electrodes prepared from dispersions are usable. Whether fabrication of large electrodes by this technique will be more feasible than the use of sheet lithium remains to be shown by further tests.

Spraying of lithium dispersion was also investigated as a method of preparing large area lithium anodes. Only low metal concentration dispersions could be sprayed, but the low concentration of lithium metal in these dispersions necessitated large spraying

*H. F. Bauman, Limited-Cycle Secondary Battery Using Lithium Anode, Final Report, Contract No. AF 33(657)-11709, Lockheed Missiles & Space Company, Palo Alto Calif., 1964.

times, and the gun became clogged before an appreciable deposit of lithium was obtained. As the proper viscosity and particle size range of the dispersion required for a successful spraying method are essentially empirical and are limited by the mechanical properties of the apparatus, a lengthly experimental program appears to be necessary before spraying can be effectively used as a method of electrode preparation.

To investigate another method of electrode preparation, a device was assembled for preparing anodes by coating metal grid with lithium dispersion and then removing vehicle liquid by vacuum. A template of depth equal to the desired electrode thickness was positioned on the bottom of a Buckner funnel. In the first trial, commercial dispersion was used in as-received condition, but this proved to be too thick, due to rapid separation, for easy even deposition, and best results were obtained with a 1:1 mixture of dispersion and hexane, deposited with a large-bore (3/32-in. needle) syringe. The deposited lithium may also be washed with propylene carbonate and the PC removed by vacuum before pressing. A trial anode prepared by this method on 4/0 nickel X-mesh and pressed at various pressures indicated that prepressing of more than 500 lb/in.² is needed to handle the anode in preparation with minimal danger of deposited lithium shifting on the backing, and that welding of the lithium occurs at approximately 2,000 lb/in.².

It is evident that sheet lithium and pressed lithium dispersion have about the same polarization. Extremely light pressing or the addition of another component (e.g., nickel) with the lithium might give reduced polarization. Utilization values have not been obtained. Of the methods tried for making a dispersion electrode, the filter cake method appears to be the simplest and most easily controlled.

2.4 COBALT TRIFLUORIDE CATHODE STUDY AND CELL TESTS

2.4.1 Polarographic Study of Cobaltic Fluoride

The study of reactions of CoF₃ as a cathodic material is of interest in establishing the reaction path, the reversibility of electrode reactions, and reactant-electrolyte interactions. A polarographic study of the reduction of cobalt salts was conducted by the use of a Sargent Model XV Recording Polarograph with a rotating platinum microelectrode for the working electrode. The reference electrode was constructed from a silver screen which was suspended in one chamber of a hydrogen cell and connected to the other chamber containing the platinum microelectrode by a tube with a glass frit. After introduction of the electrolytes into the hydrogen cell, oxygen was removed from the working electrode chamber by bubbling argon through the system, and a slow stream of argon was used during the polarographic run to prevent resolution of oxygen or water. An oxygen reduction peak was found at -0.33 V for the 1M NaPF₆-dimethyl sulfoxide electrolyte used, which was removed by argon bubbling.

The studies were performed with dimethyl sulfoxide (DMSO), since it is superior to propylene carbonate as a solvent for ionic salts. Solutions of CoF₃ and CoCl₂ were

prepared. The CoF_3 as received was a brown powder which formed a pink solution in DMSO, although of very low solubility. The CoCl_2 hydrate was dehydrated with thionyl chloride to form a dark blue powder. A 0.03 mole-solution in DMSO was of a deep blue color.

The solubility of CoCl_2 was determined by titration of chloride ion by the modified Volhard technique. CoF_3 also reacts with potassium iodide to form iodine; however, none was found in soluble form, and the pink color of the CoF_3 -DMSO solution is due to Co^{+2} -water impurity. Addition of water to the CoCl_2 -DMSO solution changed the color of the solution from blue to pink. Addition of LiF powder to CoF_3 -DMSO solution did not increase the solubility of the Co species, indicating no stable fluoride ion complex compound formation in the system. The dimethyl sulfoxide used in solution preparation was vacuumed distilled and had a specific conductivity of $5 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$. The base electrolyte was formed by addition of NaPF_6 to DMSO, forming a 1-mole solution. The final electrolyte contained traces of water, either from the NaPF_6 or absorbed during makeup. The results of the polarographic tests are summarized in Table X.

Table X

POLAROGRAPHIC TEST DATA OF COBALT SALTS

Cell: $\text{Ag}, \text{Ag}^+ | \text{NaPF}_6\text{-DMSO} | \text{Platinum Microelectrode}$

<u>Material</u>	<u>Half-wave potential $E_{1/2}$</u>	<u>Electrons/mole reaction n</u>	<u>Waves</u>
CoF_3	None obtained	—	—
CoCl_2	0.02	2	One, diffusion current is proportional to concentration

The number of electrons per mole of reaction was calculated from the polarographic voltage-current curves by the following expression for a reversible wave:

$$E_{i=3/4 \text{ ia}} - E_{i=1/4 \text{ id}} = \frac{0.056}{n}$$

No waves were obtained with the CoF_3 system, since it was not soluble in either the DMSO or LiF-DMSO solutions. A reversible reduction wave was obtained for CoCl_2 , indicating a reaction to form cobalt metal.

2.4.2 Lithium-Cobaltic Trifluoride Cell Tests

A cell composed of lithium metal and cobalt trifluoride has been of interest to the high-energy density nonaqueous battery program because of its high values of theoretical energy density (940 W-hr/lb) and high theoretical cell voltage (3.5 V). These values were obtained by assuming the reaction to be the production of cobalt metal and lithium fluoride. A summary of possible reactions of the cobalt fluorides with lithium is presented in Table XI.

Table XI
REACTIONS OF LITHIUM AND COBALT FLUORIDES

<u>Reaction</u>	<u>Standard Free-Energy Change</u>	<u>Theoretical Energy Density</u>	<u>Theoretical Cell Voltage</u>
(1) $3\text{Li} + \text{CoF}_3 = 3\text{LiF} + \text{Co}$	-244.1	940	3.54
(2) $2\text{Li} + \text{CoF}_2 = 2\text{LiF} + \text{Co}$	-131.0	620	2.84
(3) $\text{Li} + \text{CoF}_3 = \text{LiF} + \text{CoF}_2$	-113.1	484	4.90
(4) $\text{Co} + 2\text{CoF}_3 = 3\text{CoF}_2$	- 95.2	214	2.06

Cobalt trifluoride has been found to be essentially insoluble in propylene carbonate solutions of NaPF_6 and PC solutions saturated with LiF. Tests of the solubility of CoF_3 in nitromethane and in dimethyl sulfoxide indicate that Co^{+3} solubility is below the detection point, reaction with potassium iodide. The analytical procedure for the determination of CoF_3 is based on the following reaction:



The iodine which is formed is determined conveniently by titration with standard sodium thiosulphate with a soluble starch endpoint. Experimental cells have been formed with lithium anodes prepared by rolling lithium metal onto nickel or silver screen, and with CoF_3 cathodes pasted on silver or nickel expanded metal with acetylene black or cobalt metal powder for electronic conduction. The pasting has been done either with toluene or with propylene carbonate without use of a binder. Cells were formed with two lithium electrodes placed around a single cobalt fluoride electrode and with glass fiber mat separators around each electrode. A reference electrode composed of lithium formed on metal screen was inserted between the lithium and CoF_3 electrodes. The cells were placed in a polyethylene container, the electrolyte added (1-mole propylene carbonate- NaPF_6 solution), and the cells impressed with plastic blocks. The runs were conducted in an argon atmosphere dry box in order to minimize the inclusion of water. The results of the cell tests are summarized in Table XII.

Table XII
LITHIUM-COBALTIC TRIFLUORIDE CELL TESTS

Cell No.	OCV	Current (ma)	Area (cm)	Initial V*	Capacity to 2 V	Efficiency (%)
129	2.8	6	40	2.6	0.003 AH	0.3
130	3.5	6	40	3.3	0.006 (drop to 2 V plateau)	1.5
131	3.4	6	400	3.3	0 (immediate drop to 1.3 V plateau)	0
136	—	6	58	2.6	0.008	8
137	—	6	58	2.6	0.012	12

*Reference to cathode.

Each cell contained electrodes prepared with 90% CoF_3 + 10% acetylene black, except for cell 131 which was prepared with 66% CoF_3 + 33% Co powder. The electrodes used in cells 129 through 131 were pasted with a dried toluene vehicle, vacuum dried at 100° C to remove toluene, and finally heated over argon at 200° C. The electrodes used in cells 136 and 137 were prepared with vacuum-distilled propylene carbonate as the vehicle for pasting and used in the cell without drying. The efficiency of the cathodes was calculated from the ratio of the AH capacity obtained above 2 V to the amount of the CoF_3 in the electrode expressed in ampere hours for two equivalents per mole reaction. The final OCV of cells after the run was initially 1.0 V and rose to 2.6 V after a 72-hr stand. For purposes of the efficiency calculations, it was assumed that the cells spontaneously reacted CoF_3 with formed Co to make CoF_2 and electrochemically reacted the CoF_2 to form the final Co metal product. In all cases except 131, in which no test was made, the existence of cobalt metal as an end product was demonstrated by the presence of magnetic black solid material which was separated from the electrodes after the run.

Analysis of extra electrodes prepared with those which were run in the cells indicated that loss of CoF_3 occurred during the forming and drying operations. CoF_3 is reactive with traces of water, forming the CoF_2 , HF, and oxygen. The initial open circuit voltages of 3.5 V measured indicate that reaction (1) could occur. However, on passage of current and formation of cobalt metal, the cell potentials fall to 2.4 V or less and after run rise to 2.6 V, a value close to that which would be expected from

reaction (2). This sequence of cell potentials could be due to the spontaneous reaction of CoF_3 with Co as outlined by reaction (4) and the following electrochemical reaction of CoF_2 to form more cobalt metal as a final product. The fact that no observation of cells with 4.9 V has been made indicates that reaction (3), the electrochemical reaction of lithium and CoF_3 to form CoF_2 , does not occur. These studies have been conducted with cells run at constant current, and observations of the cobalt trifluoride electrode voltage versus lithium reference have been made as a function of time.

Additional cell tests were made with cobaltic fluoride cathodes with silver flake, cobalt metal powder, and acetylene black as conductive additives to the cathode powder. All cathode powders contained 70% CoF_3 and 30% additive and were ball milled for 4 hr. The dry powder containing silver flake was made into a paste with propylene carbonate, and the other two compositions were mixed with NaPF_6 -propylene carbonate electrolyte to form a paste. The wet paste was spread on nickel expanded metal grids when cobalt metal was the addition and on silver expanded metal grids when acetylene black or silver flake were added. Cells were constructed with the undried cathode, sheet lithium anodes, and glass fiber paper separator in triple-laminated polyethylene-aluminum foil-Mylar bags. A bag-type cell is shown in Figure 29. NaPF_6 -propylene carbonate electrolyte was added, and the bags were heat sealed through the electrode tabs. The cells were discharged in series at a 4 ma (1 ma/in.²) rate with the discharge curves shown in Figure 7. No long sustained discharges were obtained, and it is not clear whether there is reaction between the CoF_3 and the conductive additive, or whether the differing voltages simply reflect differing polarization. Similar cells with cathodes containing silver flake as an additive and NaPF_6 -PC were discharged at 0.32 ma/in.² in a 100° F constant-temperature chamber. An extended discharge, shown in Figure 8, was obtained at about the 3.0-V level.

Figure 8 also shows the discharge curves of cells with filter cake cathodes and 1-mole LiClO_4 -PC electrolyte. The cathodes were prepared from 80% CoF_3 , 10% graphite fiber prepared from chopped graphite cloth, 5% graphite flake, and 4% acetylene black. The dry ingredients were mechanically mixed in a blender with propylene carbonate and then filtered on a rectangular filter. The cake was sandwiched in a U-folded expanded nickel grid and assembled in bag-type cells without further drying. Cells were discharged at 0.3 and 1.5 ma/in.². The discharge curves shown in Figure 1 have two plateaus at the low rate at 3.1 to 3.25 and 2.3 to 2.6 V. At the high rate, a somewhat erratic but rapid drop in voltage occurred to somewhat of a plateau at about 2.5 V. There was approximately 4.0 gm of CoF_3 in the cathodes of these cells, which were discharged at 2.4 and 12 ma, respectively (two sides of a 2 by 2 electrode). This was equivalent to 2.7 A-hr per electrode or about 15% utilization at the lowest current density and 23.5% utilization at 1.5 ma/in.² to a 2.0-V endpoint for the cell.

Bag-type Li-CoF₃ cells with NaPF_6 -butyrolactone electrolyte discharged at laboratory ambient temperature at 0.25 ma/in.² showed a cyclic voltage change between 3.0 V to 2.5 V, which was evidently the result of temperature change. This indicates considerable temperature sensitivity of the possible cell reactions and the polarization involved in these reactions.

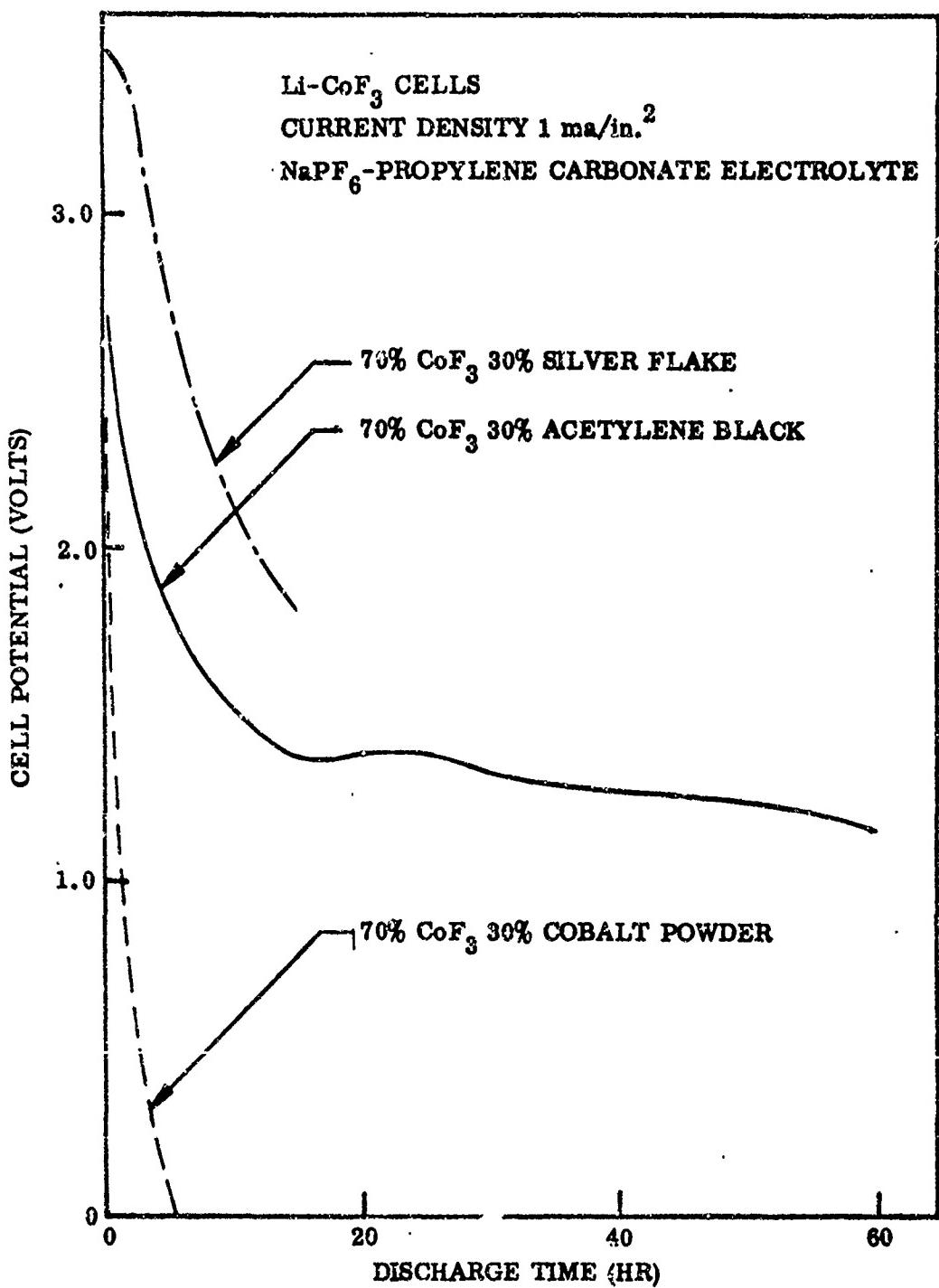


Figure 7 Cell Tests With Cobaltic Trifluoride Cathodes

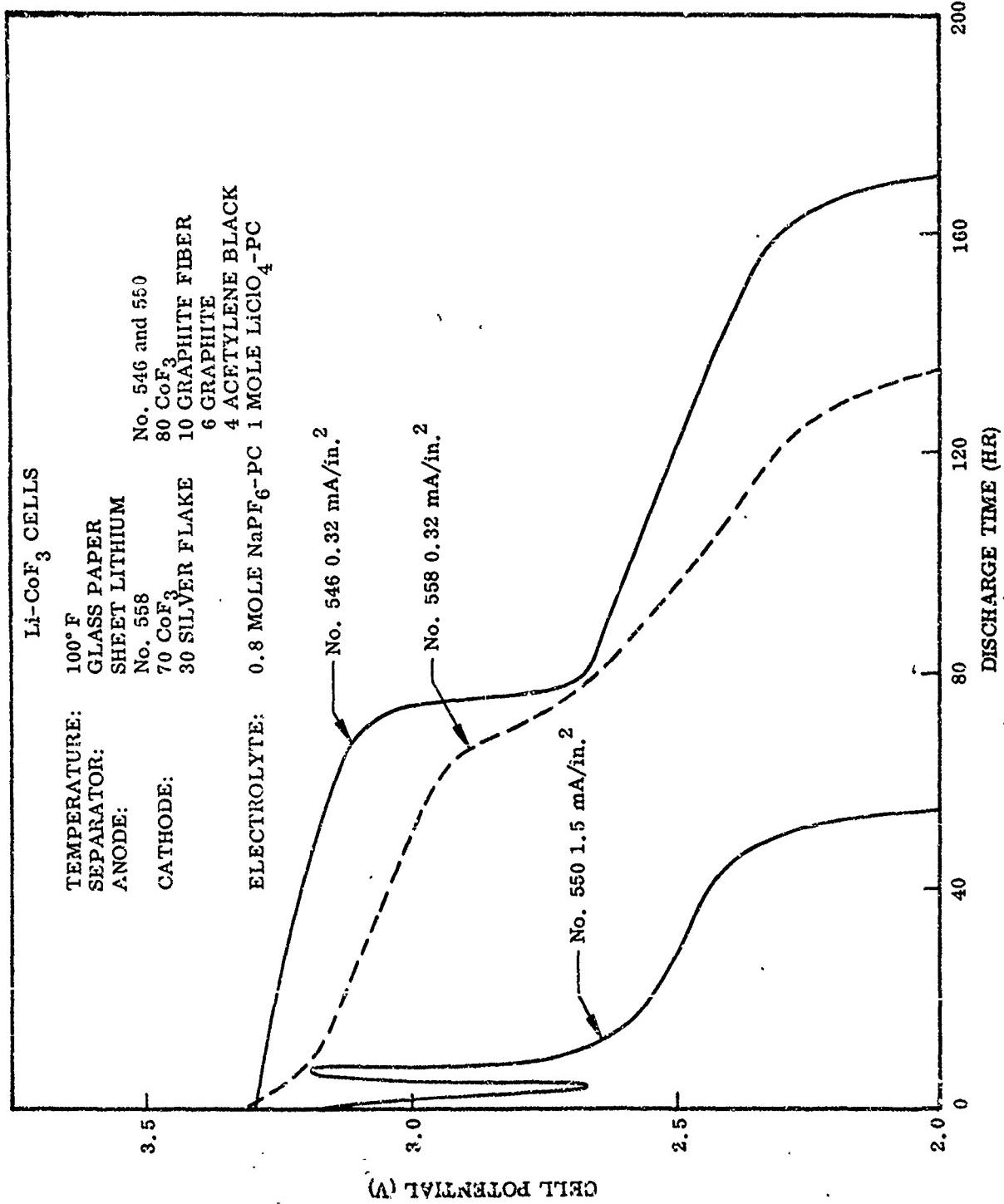


Figure 8 Discharge of Lithium Cobaltic Trifluoride Cells

2.5 CUPRIC FLUORIDE CATHODE STUDY AND CELL TESTS

2.5.1 Polarographic study of Cupric Fluoride and Chloride

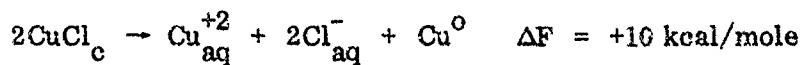
Using the techniques discussed in subsection 2.4.1 a polarographic study was made of CuF_2 and CuCl_2 . The CuF_2 was used as-received and was a grey-white powder which formed a light blue-green solution in DMSO and had a concentration of 0.07 mole when saturated. The CuCl_2 was prepared as a golden brown powder by reaction of the hydrate with thionyl chloride. Its solution in DMSO was yellow-green and contained 0.15 mole of the salt when saturated. The concentration of soluble copper species was determined by reaction with potassium iodide and titration of the resulting iodine with standard sodium thiosulfate solution. A summary of polarization data obtained with these solutions is shown in Table XIII.

Table XIII
POLAROGRAPHIC TEST DATA OF CUPRIC SALTS

Cell: $\text{Ag}, \text{Ag}^+ | \text{NaPF}_6\text{-DMSO} | \text{Pt Microelectrode}$

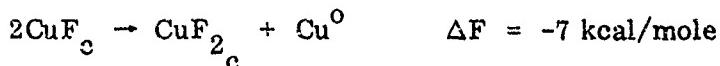
Material	Half-wave potential $E_{1/2}$	Electrons/mole reaction n	Waves
CuF_2	0.24	1	One, id proportional to concentration
CuCl_2	0.05, 0.45	1, 1	Two, id proportional to concentration

Two polarographic waves were noted in the reduction of CuCl_2 to form copper metal (visually observed on the platinum). Each wave was reversible with a single electron transfer. Aqueous cells with copper ions - $\text{Ag}^+ | \text{Cu}^{+2}$, Cu^0 and $\text{Ag}, \text{Ag}^+ | \text{Cu}^{+1}$, Cu^0 yield theoretical voltages of 0.46 and 0.28 V, respectively, which are close to the values measured for half-wave potential for the $\text{CuCl}_2\text{-DMSO}$ system, 0.45 and 0.05 V, respectively. Two waves may be obtained for CuCl_2 systems if CuCl is a stable compound and does not disproportionate. The following reactions are not thermodynamically feasible:



Only one polarographic wave was obtained from the polarographic reduction of CuF_2 to form (visible) copper metal. If the reduction were reversible with one electron exchanged per mole of reaction, then cuprous fluoride would be formed and by

spontaneous disproportionation be converted into CuF_2 and copper metal. This reaction of cuprous fluoride is feasible with the following reactions:



and CuF_2 in DMSO could react similarly.

If the single wave noted for CuF_2 reduction is considered to be an irreversible wave, the following voltage-current dependent equation is applicable:

$$E_{i=3/4 \text{ id}} - E_{i=1/4 \text{ id}} = \frac{0.054}{\alpha n}$$

where α is the electron transfer coefficient (usually 0.05). An αn value of 1 would indicate an n value of 2 for an α value of 0.5, and the reduction of CuF_2 in DMSO to form copper metal would be represented as irreversible. Irreversible polarographic waves are obtained when the rates of the forward (cathodic) and reverse reactions are appreciably different, the reverse rate being very small.

Which mechanism is operable for CuF_2 reduction is not apparent from polarographic data which have been taken. If CuF_2 were reversibly reduced to CuF with a subsequent reaction to form Cu^0 and CuF_2 , then CuF_2 would be a preferred electrode material since a cell using CuF_2 would have a single discharge potential.

A study of polarization obtained with solid electrodes is necessary to determine if reversible reduction occurs with cathodic materials which are insoluble in selected electrolyte.

2.5.2 Cells Tests With Cathode Formulation and Processing Differences

All the cells with reported results were assembled in plastic-bag cells. This type of cell was simple to assemble and required no machine parts. It evolved from a polyethylene bag, with the terminal tabs sealed in place with polypropylene wax, to the type used for the majority of the tests which consisted of a polyester-aluminum-polyethylene laminated bag with the electrode tabs heat sealed in place. A typical cell is shown in Figure 29.

The first attempts to make cupric fluoride cathodes with low polarization and high utilization were concerned with pasted electrodes, which were subsequently dried and baked. The electrodes were pasted and then placed in an electrode container which was removed from the dry box to a furnace for further processing. The electrode container itself is an Inconel pot with a removable O-ring sealed cover which has a removable water cooling coil to protect the O-ring from elevated temperatures. The container is of a size to allow it to be passed into the dry box for loading and unloading. The equipment used for cathode baking is shown in Figure 9.

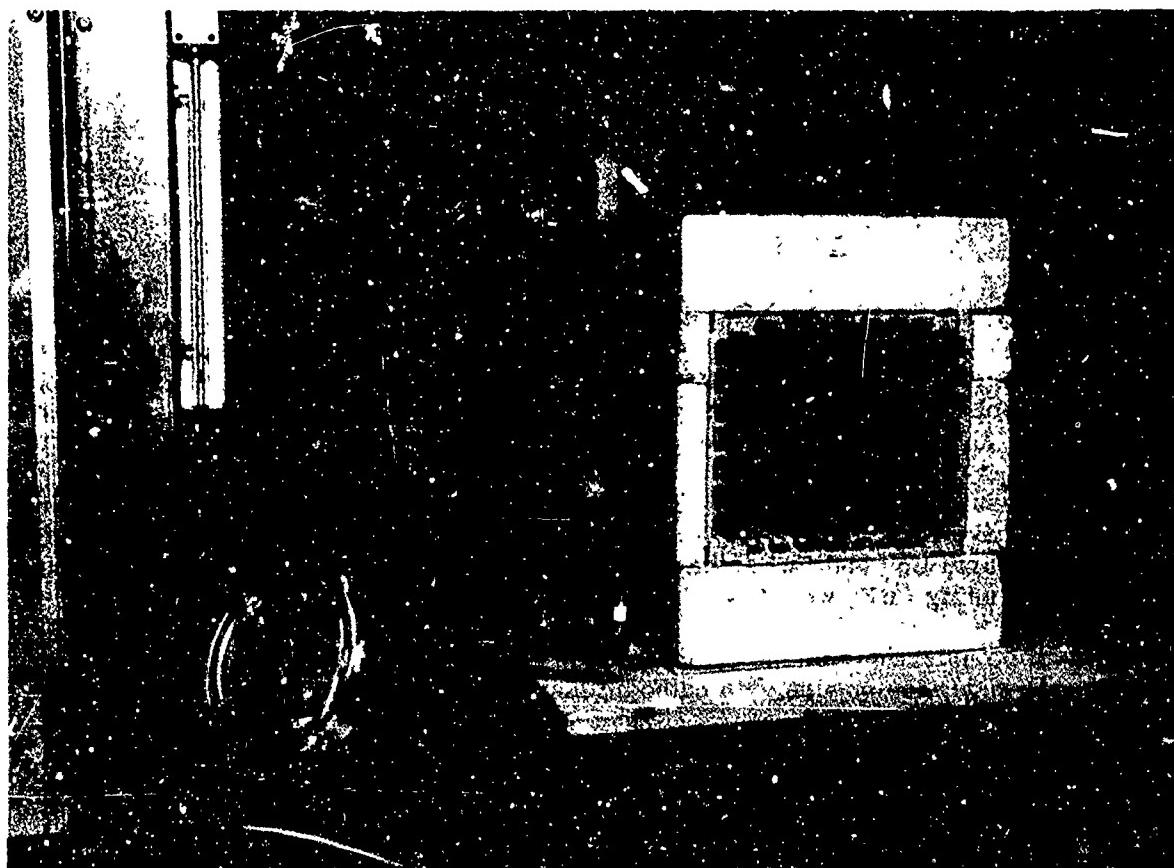


Figure 9 Cathode Preparation Container and Oven

A series of cell tests were made to evaluate the effect on cupric fluoride cathodes of the drying and baking sequence after pasting. The cells consisted of single 2 in. by 2 in. lithium anodes and cathodes assembled with glass paper separators in polyethylene bags. The electrolyte was a 0.8-mole solution of NaPF_6 in propylene carbonate. The cathodes for all cells were prepared similarly from a ball milled mix of 70% CuF_2 and 30% silver flake which was set with dry toluene and pasted on expanded copper metal. The cathodes were placed in the oven retort and vacuum dried at 100°C for 30 min, followed by a higher temperature in flowing argon for 60 min. After cooling, the electrodes were assembled in cells and series discharged at 1 ma/in.² until below 2 V/cell. A summary of the results is shown in Table XIV.

Table XIV

EFFECT OF BAKING TEMPERATURE ON CUPRIC FLUORIDE CATHODES

Cell No.	Baking Temperature (for 60 min)	Open-Circuit Voltage	Discharge Time (hr) to 2.0V
146 - 149	200°C	3.23 - 3.30	5 - 75
153 - 155	250°C	3.48 - 3.50	< 5
156 - 159	300°C	3.48 - 3.54	< 5

These tests indicate that the higher baking temperatures drastically reduce discharge time, possibly because of reaction between residual toluene and the copper fluoride. There was some indication from polarographic studies previously made that mixtures of $\text{CuF}_2\text{-CoF}_3$ might have better discharge characteristics than a single oxide.

Cathodes prepared from ball-milled 69% CuF_2 , 1% CoF_3 , 26% silver flake, and 3% acetylene black were wet with toluene, pasted on copper expanded metal, and dried 30 min in vacuum at 100°C and 60 min at 200°C in flowing argon. These cathodes were assembled with lithium anodes and glass paper separators in polyethylene bag cells and discharged at 1 ma/in.². The discharge curve of these cells (143, 144, 145) is shown in Figure 10. The periodic rise and fall of voltage in Figure 5 may be the result of temperature changes in the laboratory as it follows a 24-hr cycle, although the first increase in voltage after the initial drop had been experienced previously with similar cells. The voltage of these cells was measured with a digital voltmeter with a paper-tape printout. A Weston-type standard cell did not show a fluctuation in open-circuit voltage readings on the instrument during similar discharges, indicating that the voltage change, if thermally instigated, was the result of the temperature coefficient of the cell rather than being caused by the recording instrumentation.

Cathodes were prepared for cell tests from a 70% CuF_2 - 30% silver flake mix which was hand blended and then wet with propylene carbonate for pasting on copper expanded metal grids. These cathodes were assembled in cells similar to those previously described without further drying. The results of these cell tests (151, 152)

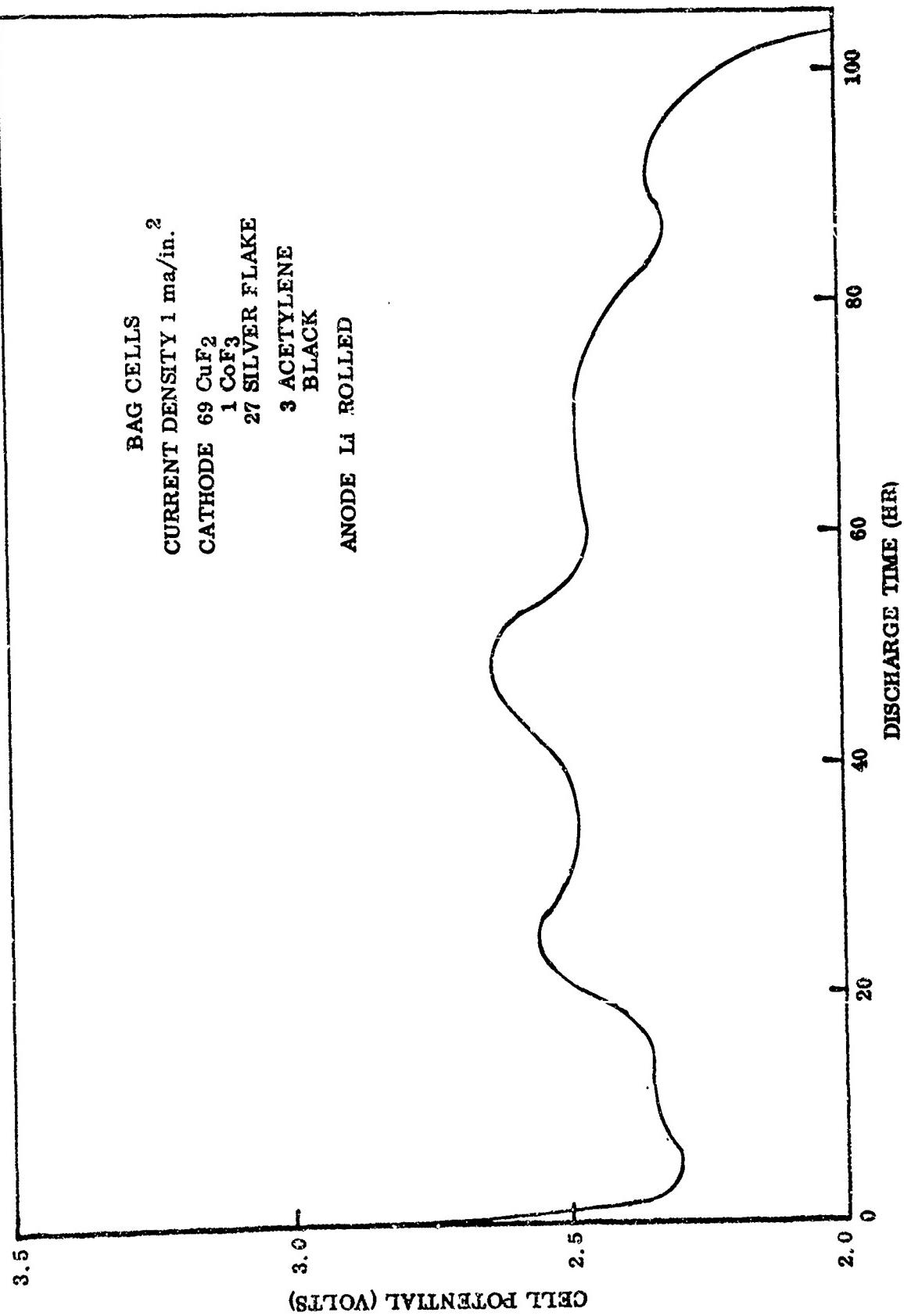


Figure 10 Discharge Test of Cells With Cupric Fluoride Cathodes Containing Cobaltic Trifluoride

are shown in Figure 11. This was the first time that extended discharges had been obtained at 1 ma/in.² above 3.0 V.

A series of cells was assembled and discharged to obtain comparative values for the effect of ball milling versus hand mixing of cathode powder, backed cathodes versus undried cathodes, and the addition of 1% CoF₃ to the cathode mix. Cathode powder mixes in the first four groups were wet with toluene and pasted on copper expanded metal. The groups were alternated in the drying retort and dried in vacuum for 30 min at 100°C and in flowing argon for 60 min at 200°C. The last four cell groups were pasted with propylene carbonate and used undried.

Table XV lists the cathode variables introduced in fabrication and the time to a 2.0-V endpoint when the cells were discharged at 1 ma/in.² constant current. All cells were assembled with a single 2 in. by 2 in. cathode and rolled lithium anode with glass-fiber paper separator and 0.8-mole NaPF₆-propylene carbonate electrolyte in plastic-bag cells. The test results indicate that ball milling is advantageous, particularly with baked cathodes, a slight improvement on this test for baked cathodes, and a general superiority of cathodes prepared from mixes containing 1% CoF₃.

In the next test groups, the proportion of CuF₂ in the cathode mix was increased to 80% and a comparison made between silver flake and copper powder as conductive additives to the cathode mix and the effect of the addition of 1% CoF₃. All cells were pasted with propylene carbonate and assembled undried. The three cathode powder compositions tested contained the following:

- 80% CuF₂ and 20% silver flake
- 79% CuF₂, 1% CoF₃ and 20% silver flake
- 80% CuF₂ and 20% Cu powder

One cell group from each cathode lot was discharged at 1 ma/in.² constant current and another lot discharged for periods of time at higher current densities. All discharges were made with a series-type constant-current regulator.

In these tests, there were inconsistent results within a group. None of the cells with copper powder-CuF₂ cathodes discharged more than a few hours. Some of the cells which had extended discharges (> 50 hr) dropped below 1.0 V initially and then recovered normal voltage in 5 to 10 hr. The best individual cells from the first two groups had 27% CuF₂ utilization to 2.5 V and 32% utilization to 2.0V. The same cells delivered 20 and 21.8 W-hr/lb to the respective endpoints.

A group of cells identical to the previous group was assembled and placed on open circuit for 39 hr before discharge under load was initiated. During this time, open-circuit voltage dropped from 3.41 - 3.51 for all groups to 3.20 - 3.25. These cells were discharged with a varied load pattern to establish voltage levels at different current densities and recovery of open-circuit voltage.

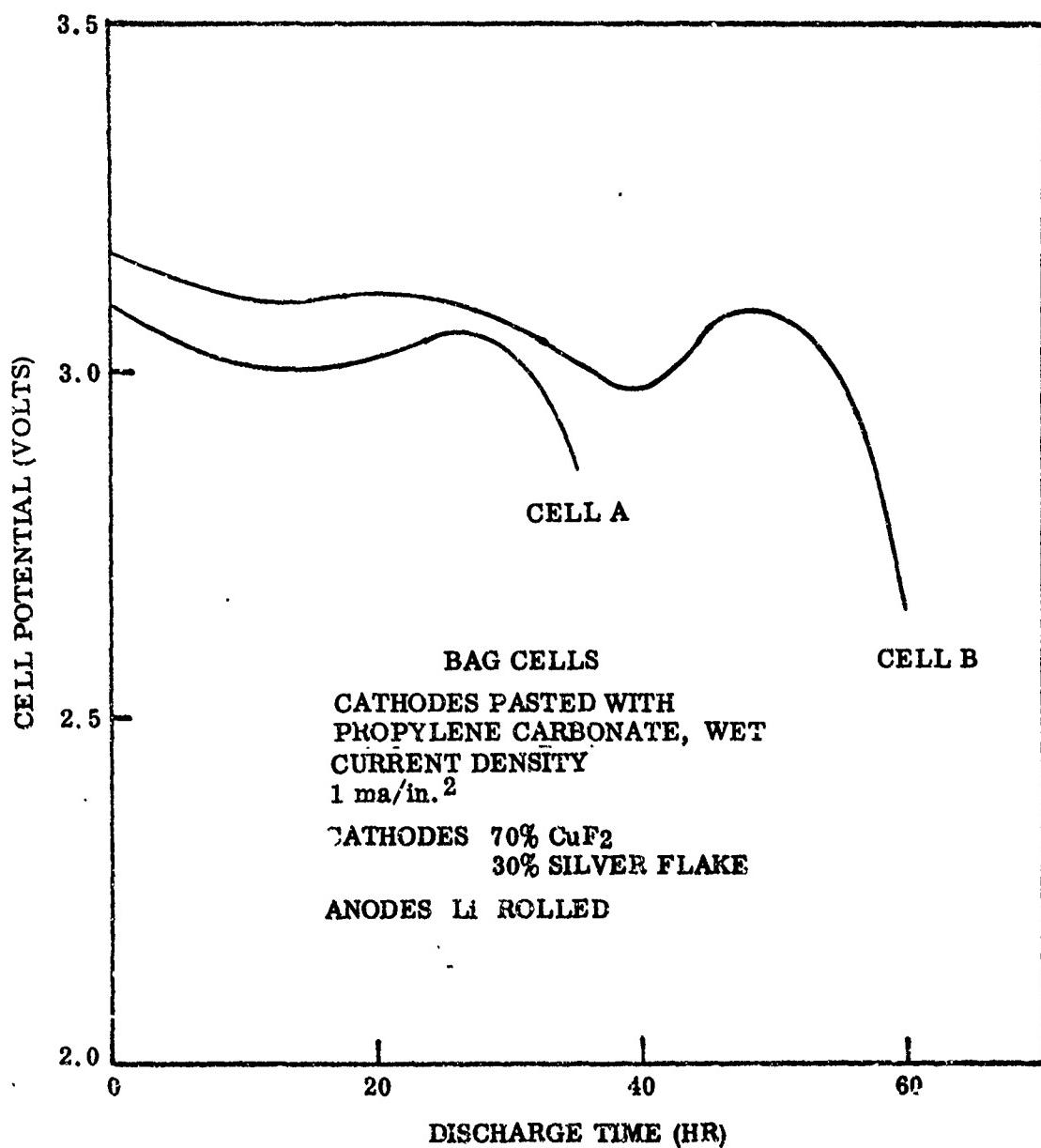


Figure 11 Test of Cells Assembled With Undried Pasted Cupric Fluoride Cathodes

Table XV
CELL TEST OF CATHODE VARIABLES

Cell No.	Cathode Composition	Powder Preparation	Cathode Preparation	Discharge Time to 2.0 volts at 1 ma/in. ²
164 - 166	69% CuF ₂ 1% CoF ₃ 27% Silver Flake 3% Acetylene Black	Ball Milled	Baked	60, 110, 110 hr
167 - 169	70% CuF ₂ 27% Silver Flake 3% Acetylene Black	Ball Milled	Baked	115, 65, 95 hr
170 - 172	69% CuF ₂ 1% CoF ₃ 27% Silver Flake 3% Acetylene Black	Hand Blend	Baked	<5, <5, 5 hr
173 - 175	70% CuF ₂ 27% Silver Flake 3% Acetylene Black	Hand Blend	Baked	<5, <5, <5* hr
176 - 178	69% CuF ₂ 1% CoF ₃ 27% Silver Flake 3% Acetylene Black	Ball Milled	Undried	80 hr
179 - 181	70% CuF ₂ 27% Silver Flake 3% Acetylene Black	Ball Milled	Undried	<72 hr
182 - 184	69% CuF ₂ 1% CoF ₃ 27% Silver Flake 3% Acetylene Black	Hand Blend	Undried	30 - 72 hr
185 - 187	70% CuF ₂ 27% Silver Flake 3% Acetylene Black	Hand Blend	Undried	>2 hr

*Dropped to 1.89, reached 2.02 after 25 hr and then dropped.

Of the nine cells in this group, only one had an immediate voltage drop with no recovery. All other cells had appreciable discharges. Another cell of the same composition had the highest consistent voltage, with over 90% of its discharge at 1 ma/in.² above 2.95 V. This cell had 22% CuF₂ utilization above 2.95 V (24% above 2.500). The longest discharge was at a 2.5-V average for the 1 ma/in.² level during the discharge following initial step discharges. This cell had 37% CuF₂ utilization to the 2.0-V level and delivered 25.6 W-hr/lb of total cell.

Cathodes were prepared with 2% LiF added to the cathode mix; the purpose of the addition was to establish an earlier electrode equilibrium during discharge by having the cell reaction product already in place. The assumed overall cell reaction is 2 Li + CuF₂ → 2 LiF + Cu, with the LiF being formed at the cathode. This would occur because of the insolubility of the F⁻ ion and its consequent reaction with the Li⁺ ion at the cathode. It was also hoped that the cell open-circuit voltage would be reduced to 3.3 V, which is the open-circuit potential of discharging cells. This would improve the voltage regulation between open-circuit and load conditions of a battery. However, initial open-circuit voltages were about 3.5 and the cell voltages dropped rapidly under load. The reason for the inability of these cells to sustain load is not clear.

One cause of large voltage losses in a cell during discharge is high resistance contact between the cathodic material and the metal electrode grid. To find the magnitude of this internal resistance for the whole cell, a bag cell with 79% CuF₂, 1% CoF₃, and 20% silver flake cathode and 0.8-mole NaPF₆-propylene carbonate electrolyte was discharged and transient voltage was observed on an oscilloscope as the load was switched on and off. A solid-state switch was used which had about 1 μ sec turn-on or turn-off time.

Figure 12 is a block diagram of the apparatus used to obtain voltage-time curves of a cell on current turn-on and turn-off. Manual operation of the push button triggers the scope trace and time delay generator. After a time interval which has been preset on the time delay generator, the pulse generator is triggered and alters the state of the flip flop. The flip-flop output controls the current switch such that when the flip-flop is in the "one" state the cell current is on and when the flip-flop is in the "zero" state the cell current is cut off. The cell voltage is applied to the upper beam and a voltage proportional to the cell current is applied to the lower beam of the dual-beam scope. Thus, repeated operation of the push button will alternately switch the cell current on and off, and the time delay allows the scope trace to show the cell voltage in the previous state as well as the transient due to the switching.

The major voltage change was a relatively slow phenomenon, as shown on Figure 13. Photographs taken at a sweep rate of 5 μ sec/cm showed substantially the same quantitative rapid drop, attributed to ohmic resistance, as those taken at a sweep rate of 5 msec/cm. The ohmic resistance observed was similar to that observed by ac resistance measurements, 5 to 10 ohm. This corresponds to 10 to 20 mV at these currents and is a relatively small factor in loss of voltage. The longer time voltage changes may be attributed to concentration polarization dependent upon diffusion of ions to the active surface of the electrode, or to effects within the electrodes.

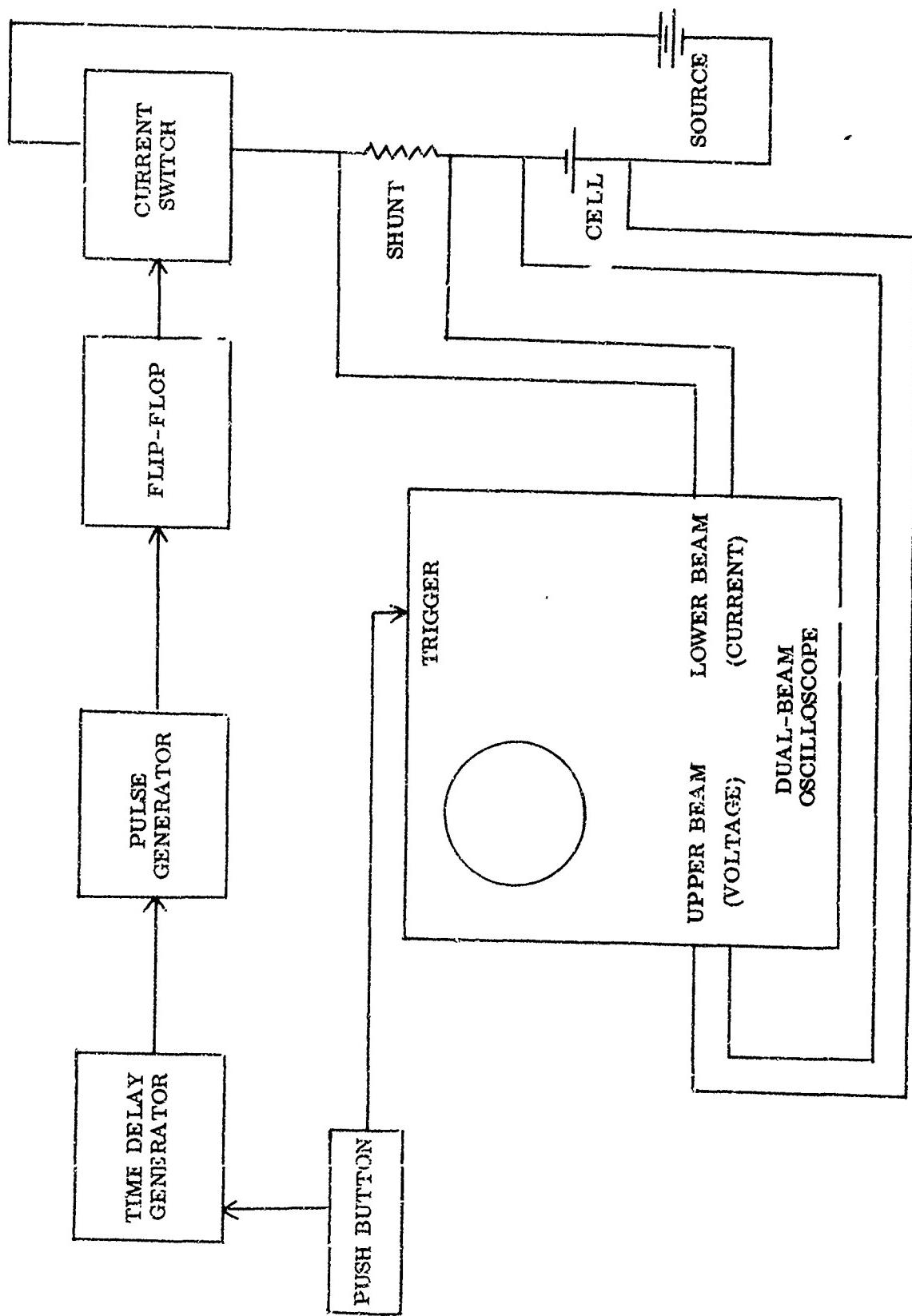
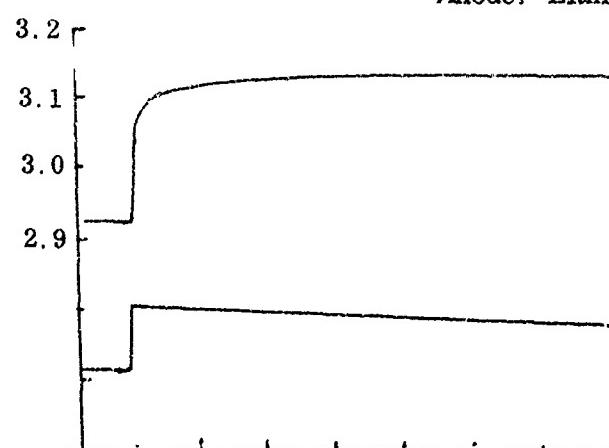


Figure 12 Block Diagram of Interrupter Circuit

CELL 368

Cathode: 79 CuF₂
 1 CcF₃
 20 Silver Flake
 Electrolyte: NaPF₆-Prop. Carb.
 Separator: Glass Paper
 Anode: Lithium Sheet

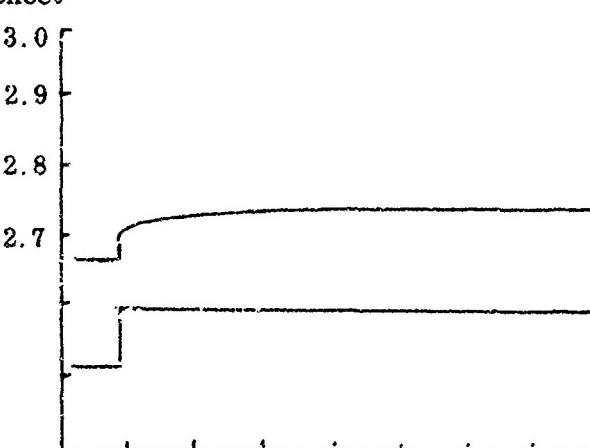


Cell 368 (After 5-min Discharge)

Turn off from 0.9 ma/in.²

5 sec/cm

0.1 volt/cm

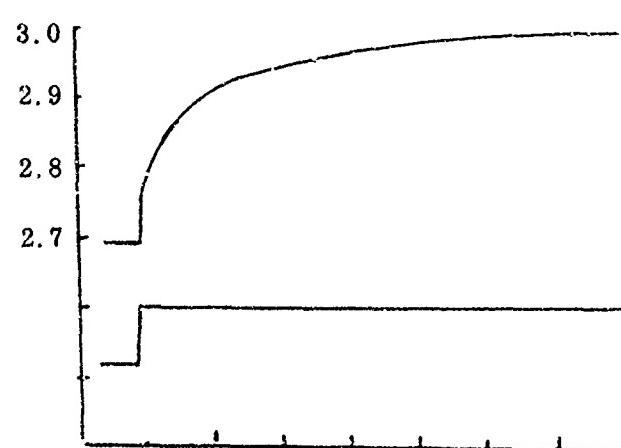


Cell 368 (After 4-hr Discharge)

Turn off from 0.9 ma/in.²

5 msec/cm

0.1 volt/cm

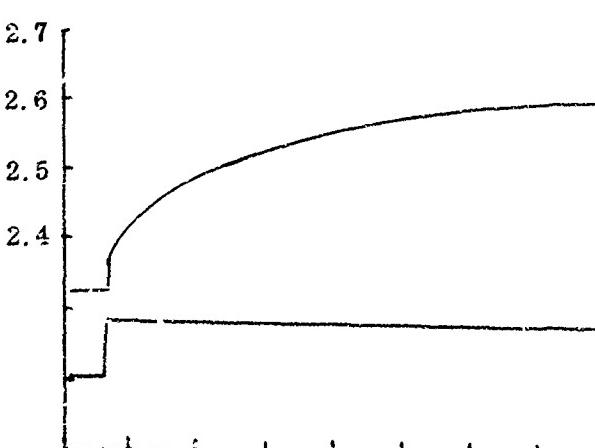


Cell 368 (After 5-hr Discharge)

Turn off from 0.9 ma/in.²

5 sec/cm

0.1 volt/cm



Cell 368 (After 13-hr Discharge)

Turn off from 0.9 ma/in.²

5 sec/cm

0.1 volt/cm

Figure 13 Transient Voltage During Current Interruption

Two cells were assembled with reference electrodes to determine individual electrode polarization during discharge. These cells had one anode and one cathode, and a lithium reference electrode about 0.06 in. wide was placed between the working electrodes. The cathodes were prepared by pasting a mixture of 80% CuF₂ and 20% silver flake on silver expanded metal. The cell potential and working electrode - reference potentials during discharge are shown in Figure 14. In this case, the steady decline of cell voltage during discharge was almost entirely due to the cathode during the first 50 hr, after which the anode made a small contribution. The reference to working electrode polarization values shown on the graph includes a resistive component because of the reference electrode location midway between the working electrodes. About 35% of the active material was used on this discharge, so the increase in polarization was not caused by consumption of reactants.

2.5.3 Cell Tests With Electrolyte Variations

Two groups of cells were assembled and tested with a series of electrolyte formulations. One group had cathodes prepared from powder containing 79% CuF₂, 1% CoF₃, and 20% silver flakes, and the other from powder with the same composition but 20% copper flake rather than silver flake. Both powders were ball-milled 16 hr, the powder wet with the appropriate electrolyte and pasted on expanded metal mesh which was silver for the silver flake mix and copper for the copper flake mix. The electrolytes used in this experiment were 0.7-mole NaPF₆-propylene carbonate, and saturated solutions of NH₄PF₆-dimethyl formamide, NaPF₆-dimethylsulfoxide, NaPF₆-butyrolactone, NH₄PF₆-propylene carbonate, and NaSbF₆-propylene carbonate. The cathodes were assembled with lithium sheet anodes rolled on expanded metal sheet paper separators in triple-laminated polyethylene-aluminum foil-Mylar bags. The bags were heat sealed through the electrode tabs after addition of the appropriate electrolyte. NH₄PF₆-dimethyl formamide was not used in the second group of tests because of indications of reaction. Different current density profiles were used for the two groups of cells. The discharge curve of the best cell from each group of three is plotted in Figures 15 and 16. Only the best cell is plotted because of the inconsistency between individual cell tests. The figures can be used for some comparison between electrolytes; although they cannot be used for absolute comparison, they can serve as a guide for future work.

Bag-type cells were also assembled with propylene carbonate based electrolyte in which both anions and cations were changed. The salts selected were lithium, sodium, potassium, and benztrimethyl ammonium hexafluorophosphates and, in addition, lithium chloroaluminate and perchlorate. Duplicate cells were assembled with a center lithium reference electrode. The discharge curves of typical cells from these groups is shown in Figures 17 and 18. Of the PF₆⁻ salts, the LiPF₆ electrolyte cells had the highest voltage discharge, but the $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$ electrolyte cells had a sustained discharge at a lower level. Disregarding the quaternary ammonium salt, the cell discharges were progressively poorer as the anion in the electrolyte became larger (with the PF₆⁻ cation). This agrees with previous cell tests with KPF₆ electrolyte, which has given consistently poor results. That these results were little influenced by the resistance of the electrolyte is shown in Table XVI by the similar values measured on the actual electrolytes used in the cells.

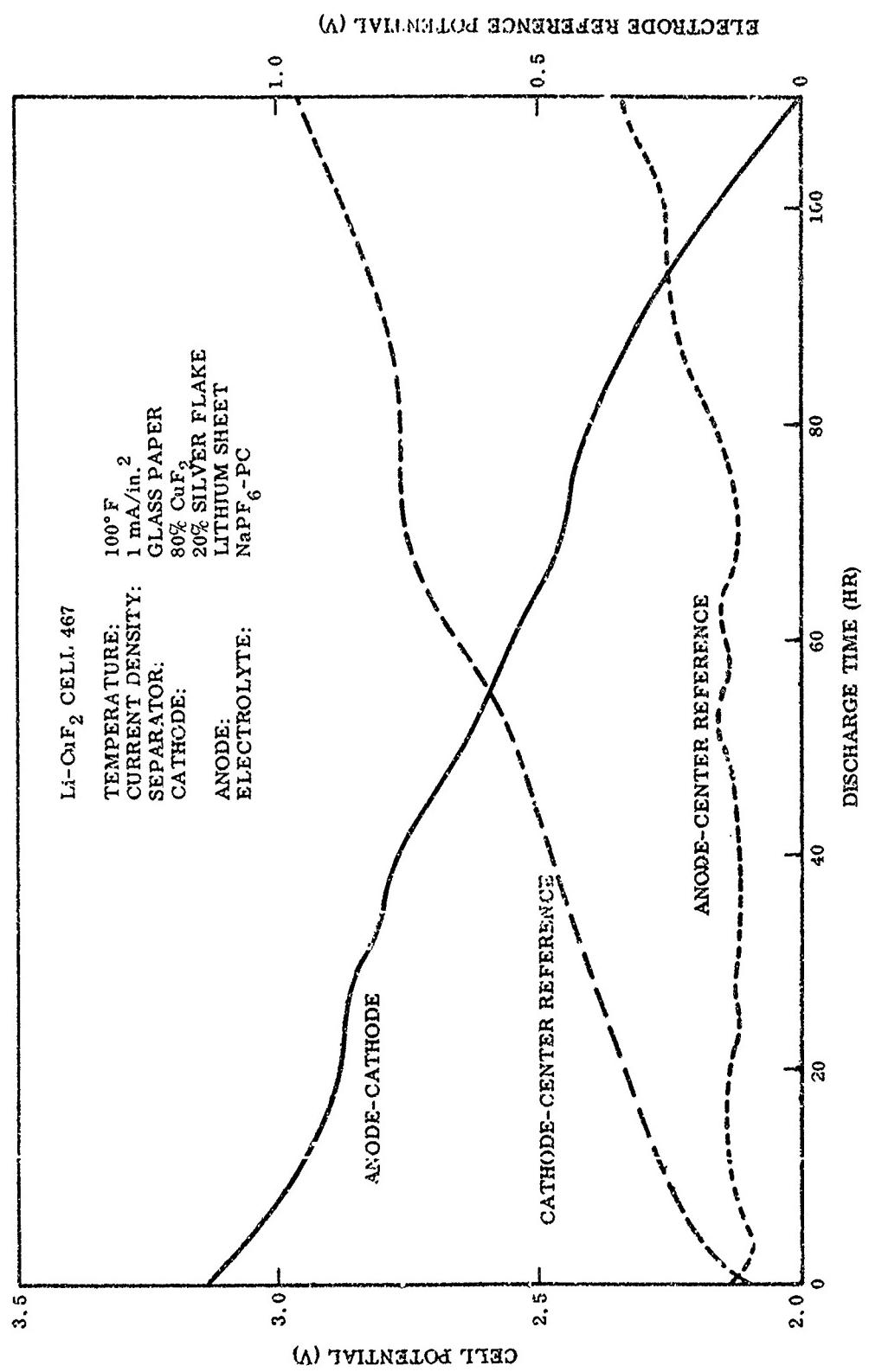


Figure 14 Discharge of Lithium-Cupric Fluoride Cell With Reference Electrodes

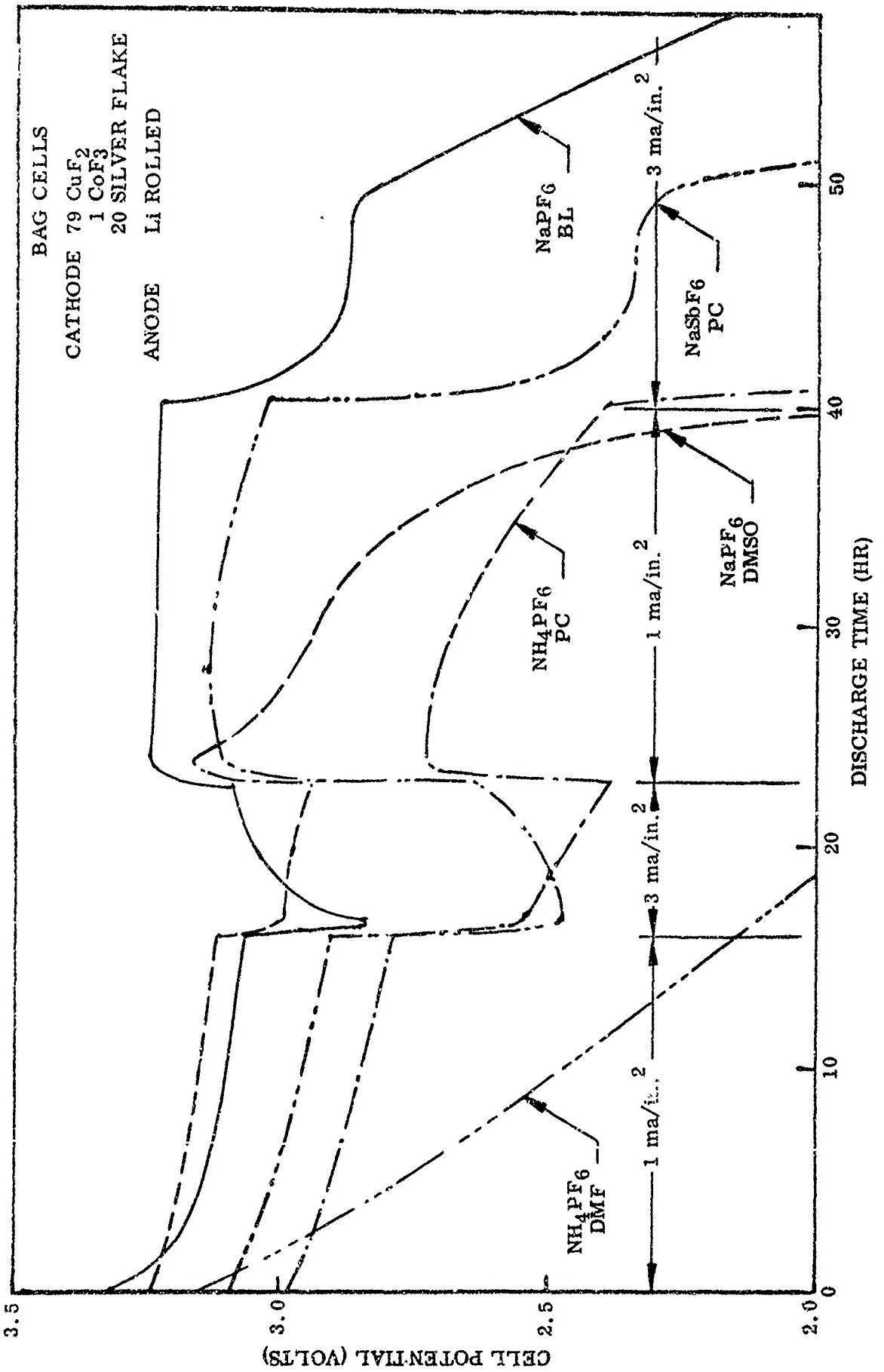


Figure 15 Cell Tests for Electrolyte Evaluation With Cathodes Containing Silver Flake

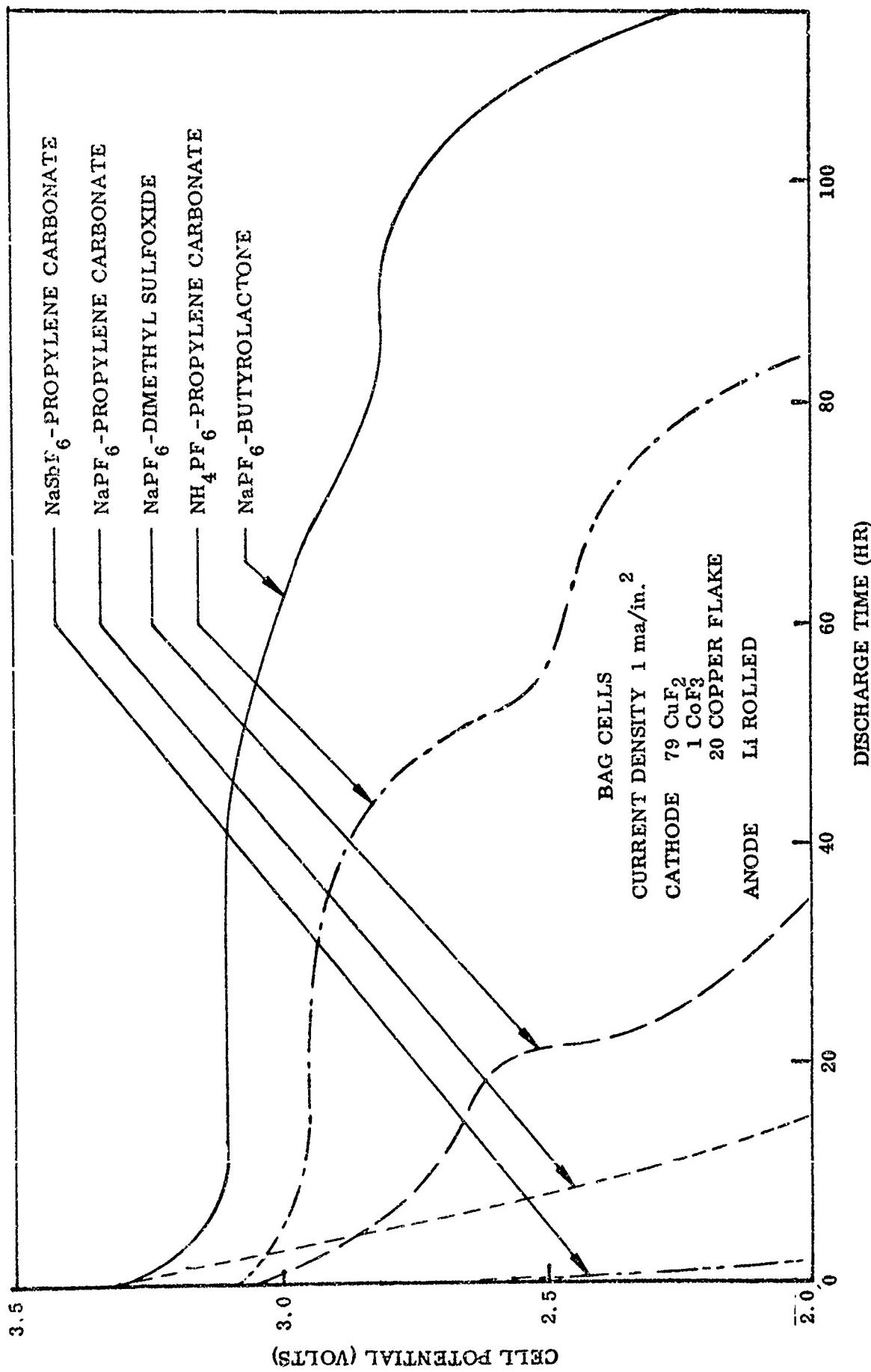


Figure 16 Cell Tests for Electrolyte Evaluation With Cathodes Containing Copper Flake

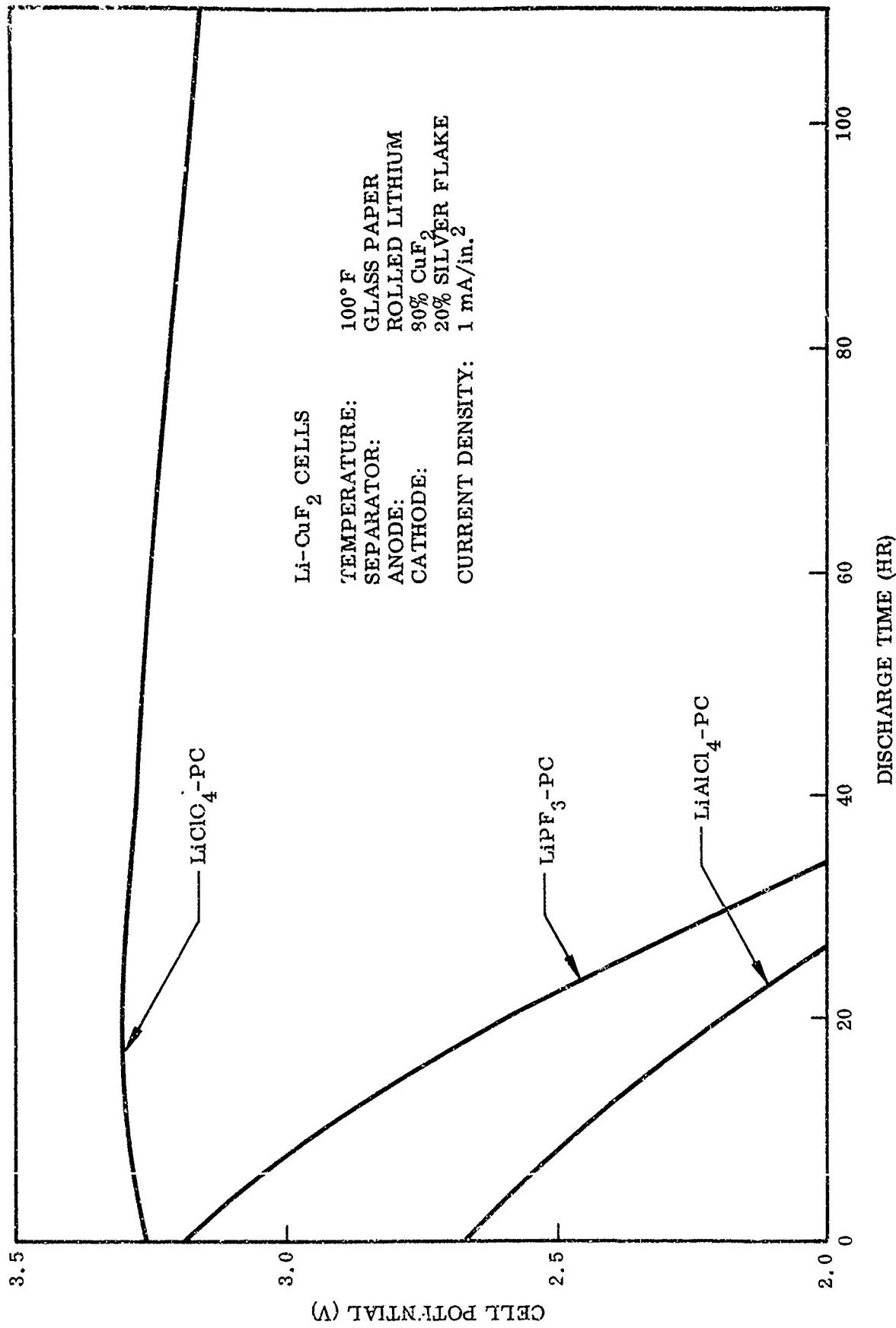


Figure 17 Discharge of Cells With Different Anions in the Electrolyte

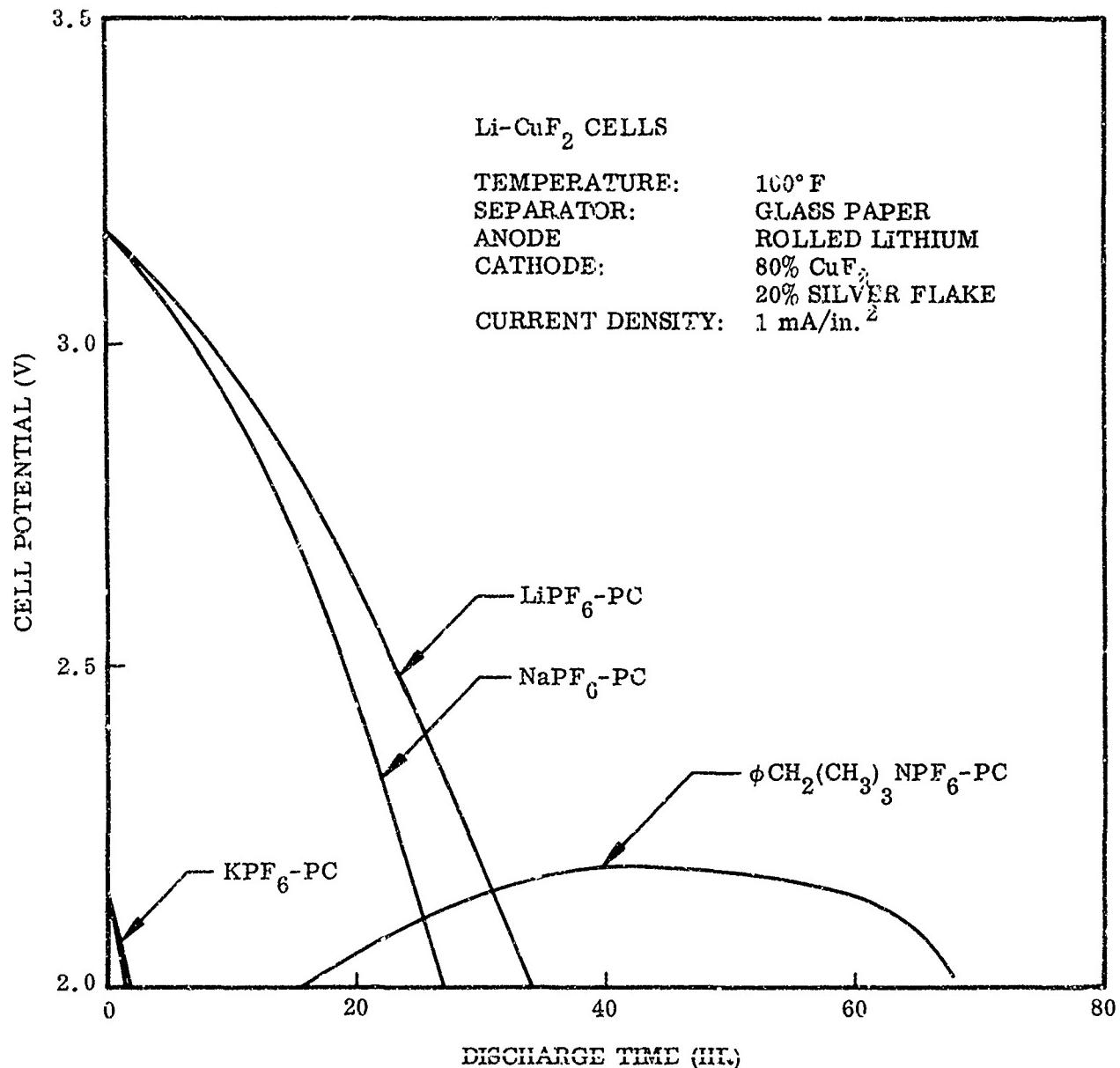


Figure 18 Discharge of Cells With Different Cations in the Electrolyte

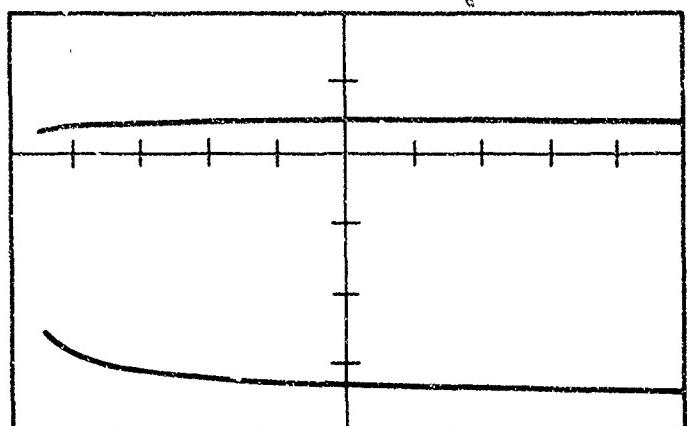
Table XVI
SPECIFIC CONDUCTIVITY OF ELECTROLYTES
USED FOR CELL DISCHARGES

Salt	Solvent	Specific Conductivity ($\Omega^{-1} \text{cm}^{-1}$)
LiClO_4	Propylene carbonate	5.7×10^{-3}
LiAlCl_4	Propylene carbonate	6.2×10^{-3}
LiPF_6	Propylene carbonate	6.1×10^{-3}
NaPF_6	Propylene carbonate	6.7×10^{-3}
$\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$	Propylene carbonate	7.2×10^{-3}
KPF_6^*	Propylene carbonate	6.9×10^{-3}

*This value from previously prepared solution.

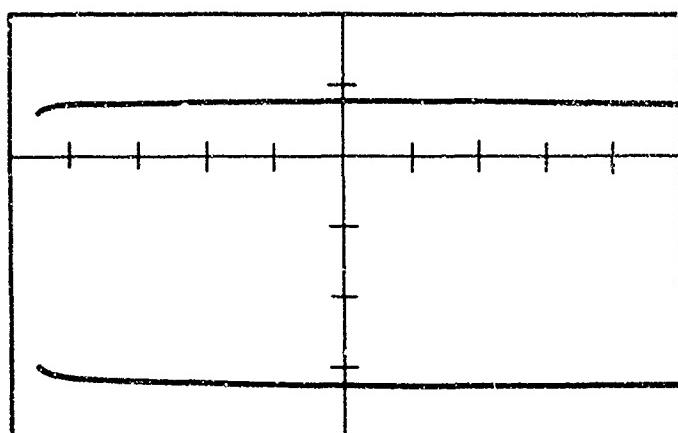
Cells with NaPF_6 -PC have previously given better results than in this test. Polarization measurements were made on these same cells by current interruption techniques after a few minutes, 2 hr, and 20 hr of discharge. The results, as photographed on the oscilloscope, are shown in Figure 19. Similar anode-reference potential curves were obtained for the alkali metal hexafluorophosphates electrolytes. Similar cathode-reference potentials were also obtained with the NaPF_6 and LiPF_6 electrolytes. However, both the KPF_6 and $\phi\text{CH}_2(\text{CH}_3)_3\text{NPF}_6$ electrolyte cells showed slower voltage recovery after initial discharge as evidenced by the small and abrupt voltage change on the oscillograms and the low cell voltage. After initial discharge, the LiAlCl_4 , LiPF_6 , and LiClO_4 based electrolytes were similar in showing a fairly rapid anodic recovery, but the LiClO_4 electrolyte showed a slower recovering cathode-reference potential. A much slower sweep would give a clearer picture of the slow recovery, but the current interruption data with the discharge curves can be correlated for the conclusions as drawn. The reference electrode on the LiClO_4 electrolyte cell shorted during discharge, and no 20-hr discharge measurement was made.

Additional cells were prepared with LiClO_4 -PC electrolyte and discharged. The discharge curves shown in Figure 20 show about twice the discharge time for a cell discharged at 1.5 ma/in.^2 compared with one discharged at 3.0 ma/in.^2 for the same A-hr capacity. However, additional discharge time was obtained with this cell at a lower current density for a total capacity of 0.94 A-hr to 2.0 V. With an average cell voltage of 2.75, this cell, with a weight of 25 gm, delivered 45 W-hr/lb. Utilization of CuF_2 was 33% for the discharge to the 2.0-V endpoint.

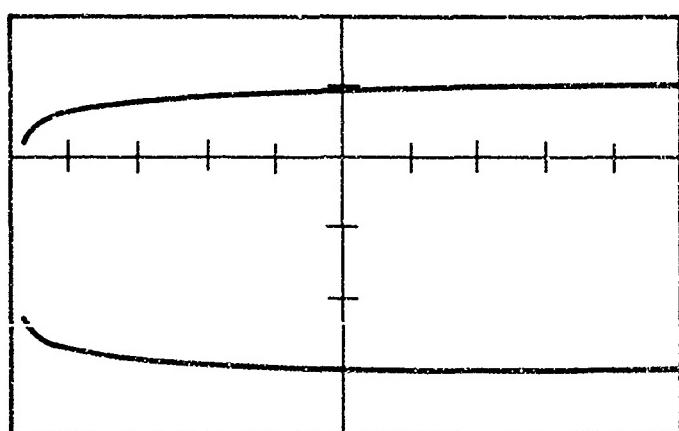


Li-CuF₂ Cell 483
Electrolyte LiPF₆-PC
Upper Trace CuF₂-Reference
Lower Trace Li-Reference
Vertical Axis 0.1 V/cm
Sweep 10 msec/cm
Current Turnoff

Initial

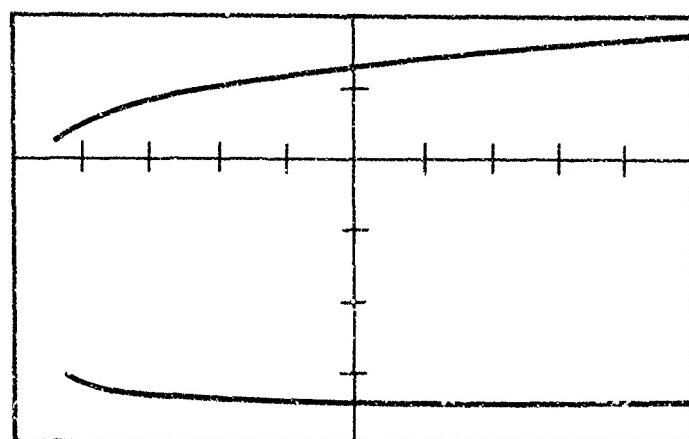


After 2-hr discharge



After 20-hr discharge

Figure 19 Transient Voltage During Current Turn-Off



Li-CuF₂ Cell 476

Electrolyte NaPF₆-PC

Upper Trace CuF₂-Reference

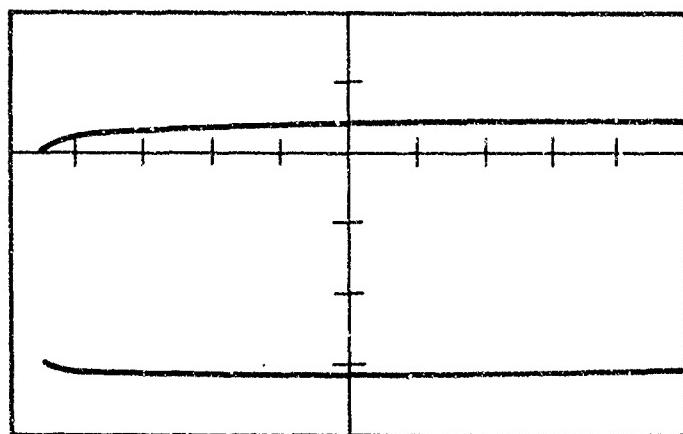
Lower Trace Li-Reference

Vertical Axis 0.1 V/cm

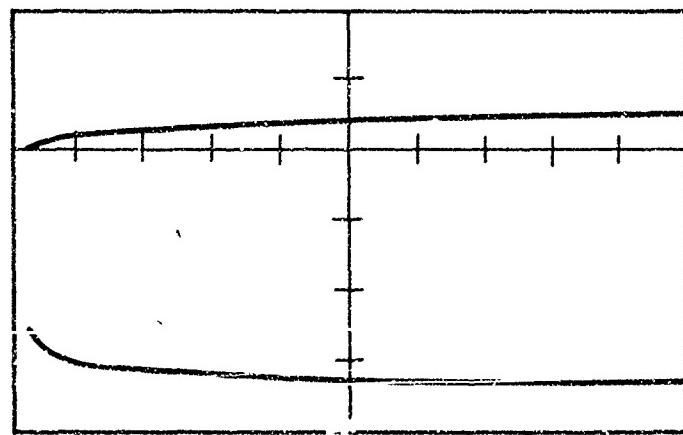
Sweep 10 msec/cm

Current Turnoff

Initial

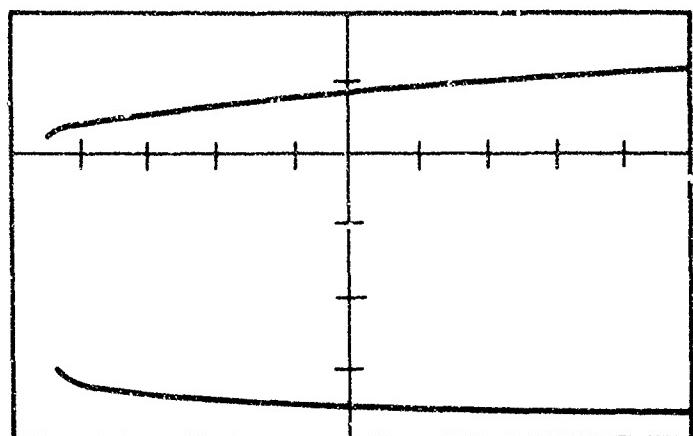


After 2-hr discharge



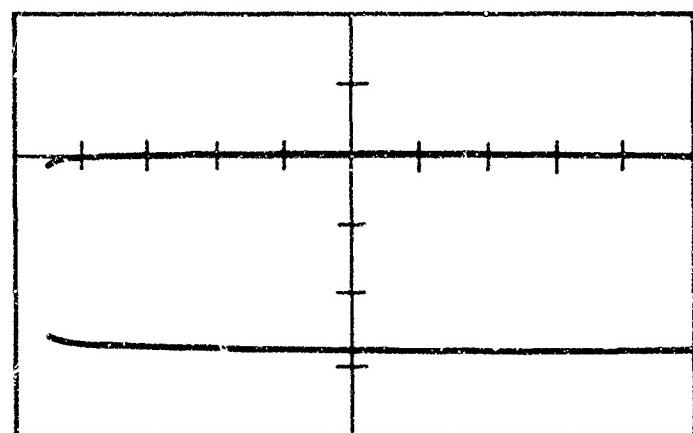
After 20-hr discharge

Figure 1^a (Cont.)

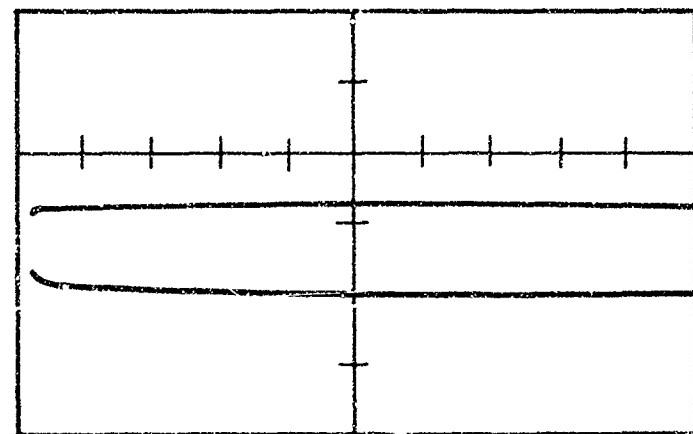


Li-CuF₂ Cell 479
Electrolyte KPF₆-PC
Upper Trace CuF₂-Reference
Lower Trace Li-Reference
Vertical Axis 0.1 V/cm
Sweep 10 msec/cm
Current Turnoff

Initial



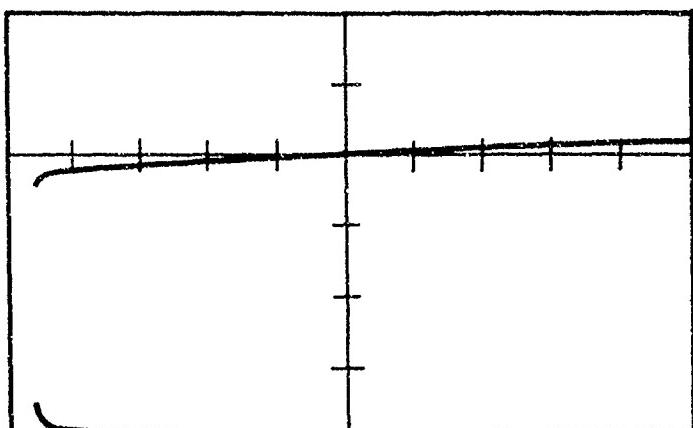
After 2-hr discharge



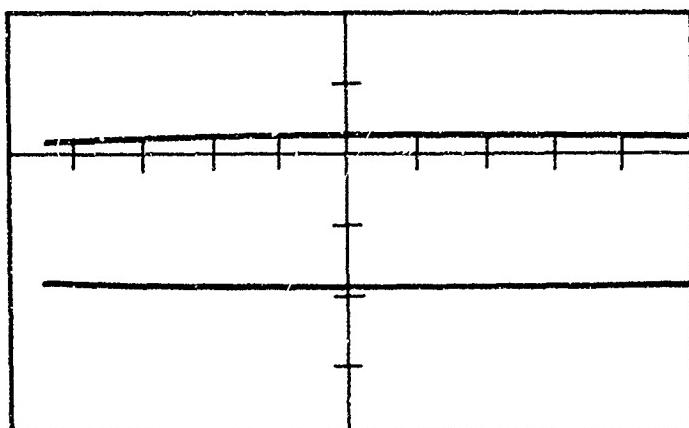
After 20-hr discharge

Figure 19 (Cont.)

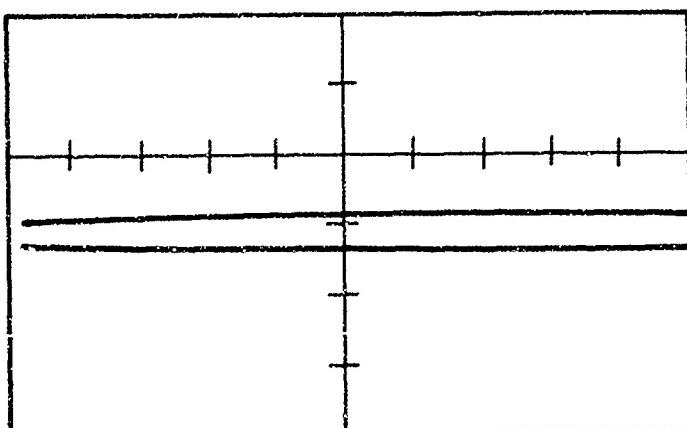
Li-CuF₂ Cell 477
Electrolyte $\phi \text{CH}_2(\text{CH}_3)_3\text{NPF}_6\text{-PC}$
Upper Trace CuF₂-Reference
Lower Trace Li-Reference
Vertical Axis 0.1 V/cm
Sweep 10 msec/cm
Current Turnoff



Initial

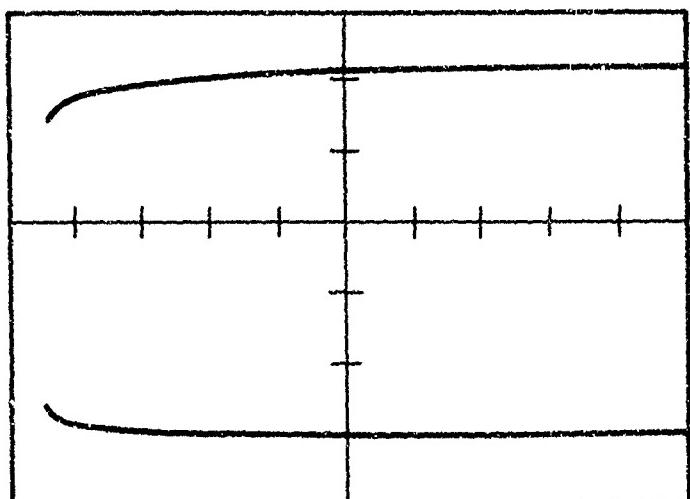


After 2-hr discharge



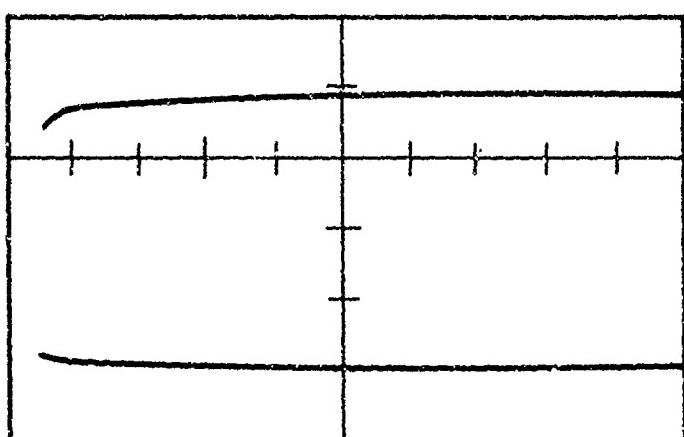
After 20-hr discharge

Figure 19 (Cont.)

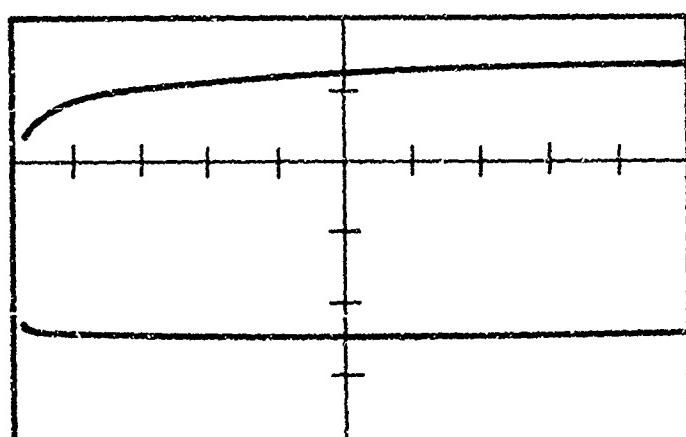


Li-CuF₂ Cell 485
Electrolyte LiAlCl₄-PC
Upper Trace CuF₂-Reference
Lower Trace Li-Reference
Vertical Axis 0.1 V/cm
Sweep 10 msec/cm
Current Turnoff

Initial



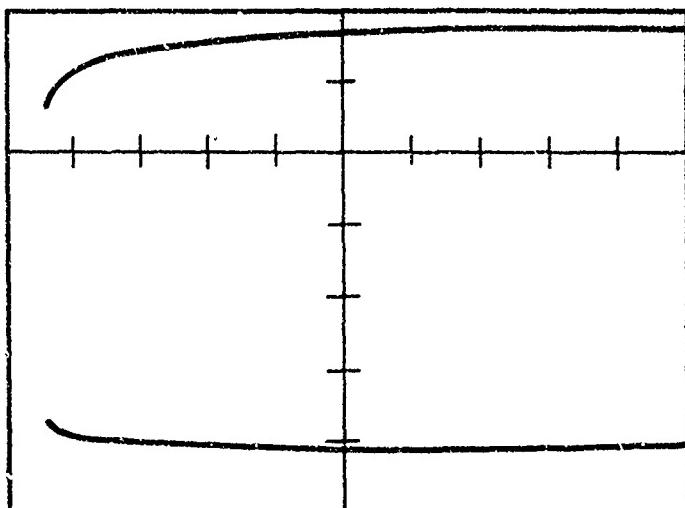
After 2-hr discharge



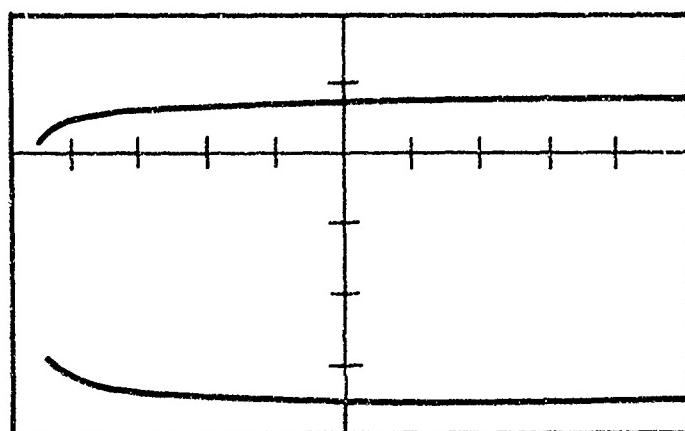
After 20-hr discharge

Figure 19 (Cont.)

Li-CuF₂ Cell 481
Electrolyte LiClO₄-PC
Upper Trace CuF₂-Reference
Lower Trace Li-Reference
Vertical Axis 0.1 V/cm
Sweep 10 msec/cm
Current Turnoff



Initial



After 2-hr discharge

Figure 19 (Cont.)

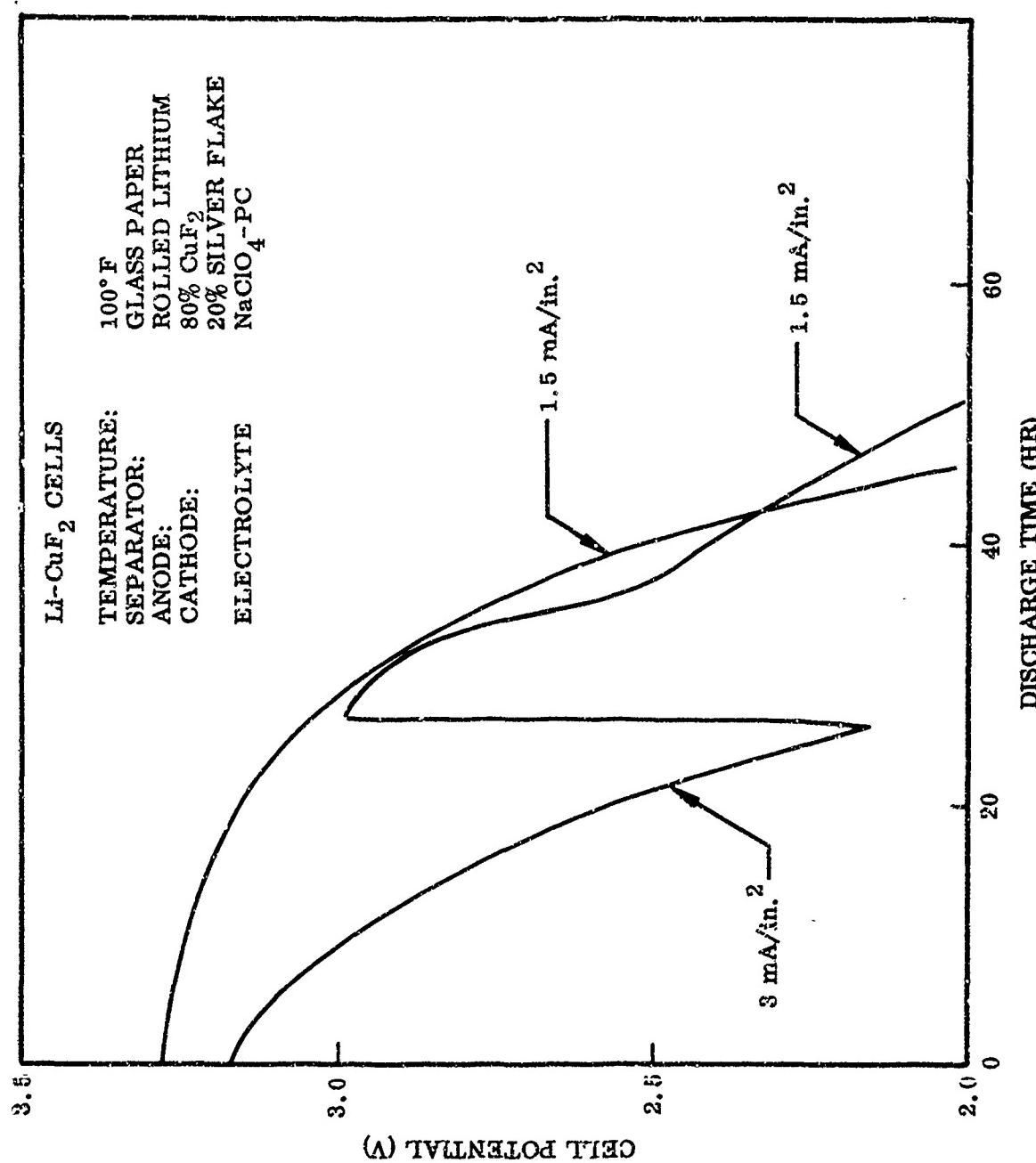


Figure 20 Discharge of Cells With Lithium Perchlorate-Propylene Carbonate Electrolyte

2.5.4 Cell Tests With Filter Cake Cathodes

Cells were prepared from cathodes prepared by a filter-cake technique rather than by pasting. In this method, the CuF_2 was wet ball milled in hexane and added to a mixture of chopped graphite fiber and powdered graphite in a blender. The graphite fiber was obtained by chopping graphite cloth. After blending, the mixture was filtered in a Buchner filter. The filter cake was cut to size and sandwiched in a U-folded expanded metal grid. Bag-type cells were assembled and discharged at 4 ma/in.^2 as shown in Figure 21. Although the discharges were relatively short, these were the first sustained discharges obtained at this current density. A rectangular filter with a perforated bottom 4 by 6 in. was welded from aluminum and used to prepare additional electrodes. A similar filter used to prepare larger filter-cake electrodes is shown in Figure 22. Typical cells assembled in a similar manner from these electrodes were discharged as shown in Figure 4.

An additional cathode mix was prepared by a similar process from 60 gm of copper fluoride which had been ball milled for 16 hr with propylene carbonate, 10 gm of acetylene black, and 10 gm of shredded graphite fibers. A portion of the mix was poured onto filter paper and copper expanded metal electron collector in the vacuum filter apparatus. The mix was washed with successive portions of hexane and of ethyl ether, cut into 2 in. squares, and enclosed by folding with the copper electron collector. The composite cathode was wrapped with glass fiber separator and placed in a cell with a single rolled lithium sheet anode. The electrolyte used in these tests was 0.7-mole NaPF_6 in propylene carbonate. Runs were made at currents from 96 ma to 4 ma, and the variation of cell voltage with cell capacity in milliamperes-minutes is presented in Figure 23. The runs at 4 ma or 1 ma/cm^2 current density had an efficiency of 37% for reaction at one electrode face. The results presented are from single electrode cell tests and show in part the variability in mix control and structure nonuniformity.

Additional cells with cathodes prepared by filter-cake techniques were assembled and tested. The goal of these tests was to increase the current density and utilization of active material during discharge and the improvement of handling of the cathode slurry.

A comparison of cells with $\text{LiClO}_4\text{-PC}$ and $\text{NaPF}_6\text{-PC}$ electrolytes is made in Figure 24. Filter-cake cathodes formulated with a variety of compositions were used in the test. The voltmeter printer ran out of paper after 40 hr of discharge, and new paper was not added until after 88 hr of discharge. With all cathode formulations, much better results were obtained with $\text{LiClO}_4\text{-PC}$ electrolyte. The best cell had 58% utilization above 3.0 V for the cell and delivered 60 W-hr/lb for actual cell weight. Somewhat more than one-third of the cell weight was electrolyte.

Other cells with filter-cake cathodes were assembled with different proportions of conductive additives. Discharge curves for these cells are shown in Figures 25 and 26. There was enough cathodic material in these cells for 180 hr of discharge at the 1.5 ma/in.^2 discharge rate and somewhat greater excess of lithium.

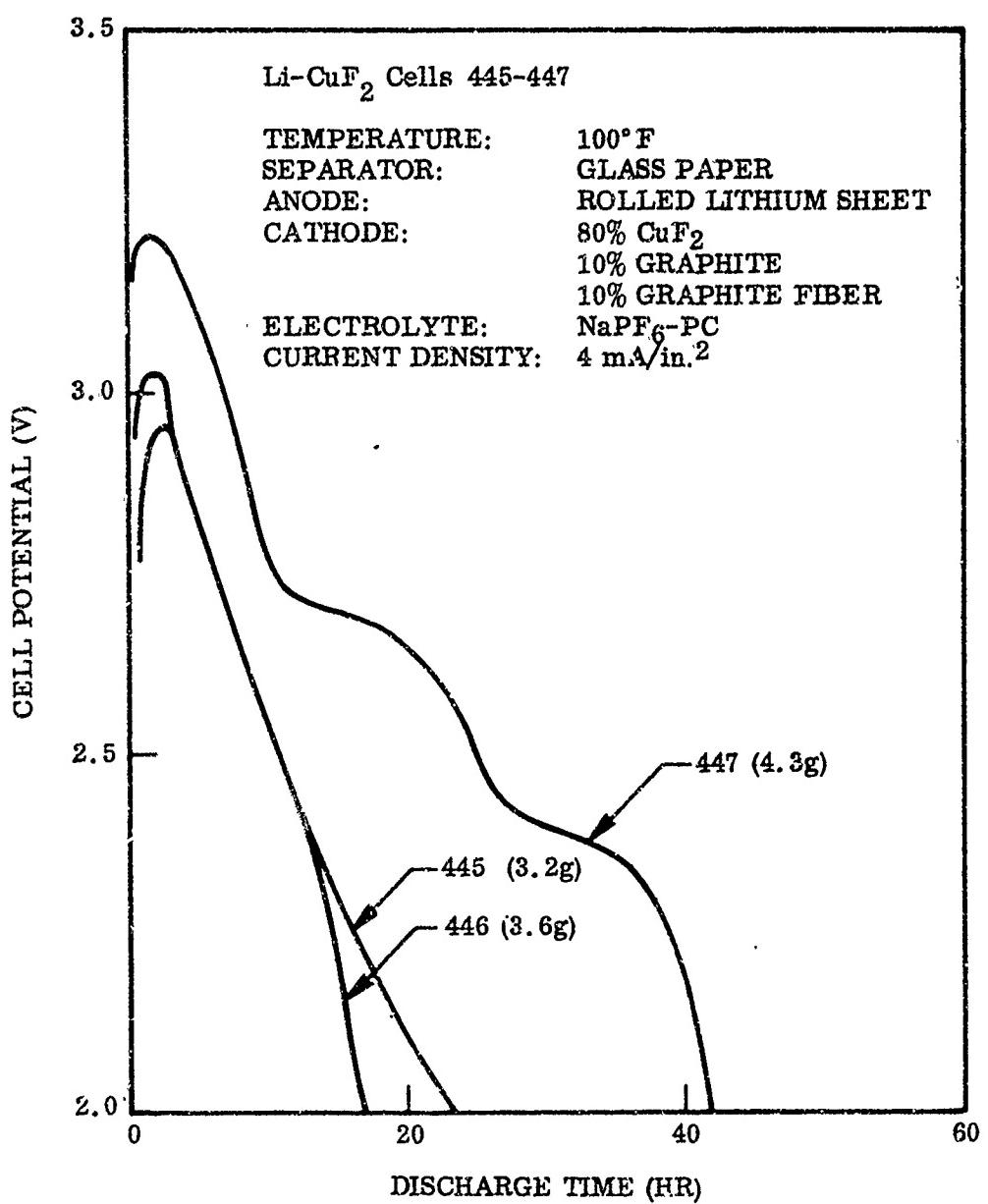


Figure 21 Discharge of Cells With Filter Cake Cathodes

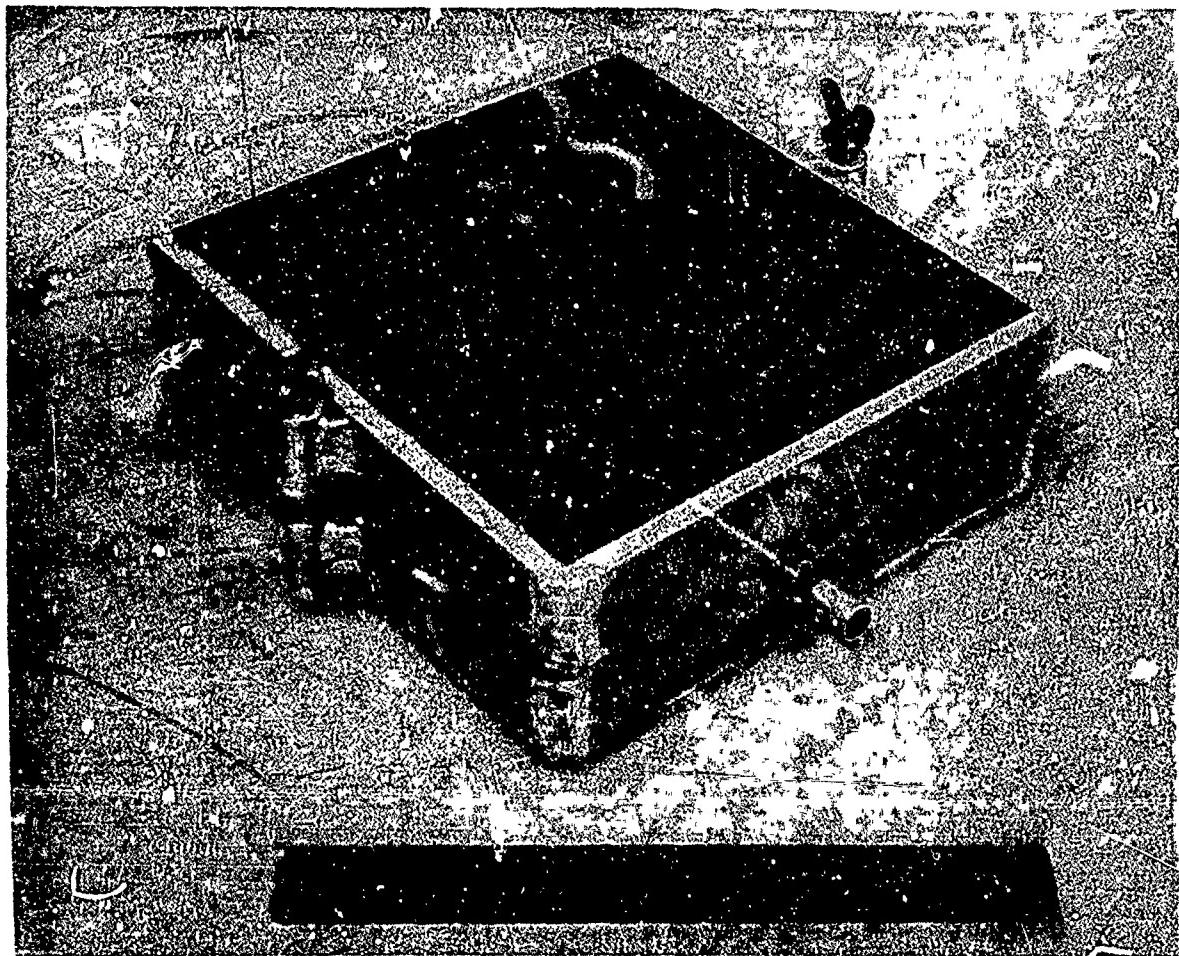


Figure 22 Filter for Preparing Filter Cake Cathodes

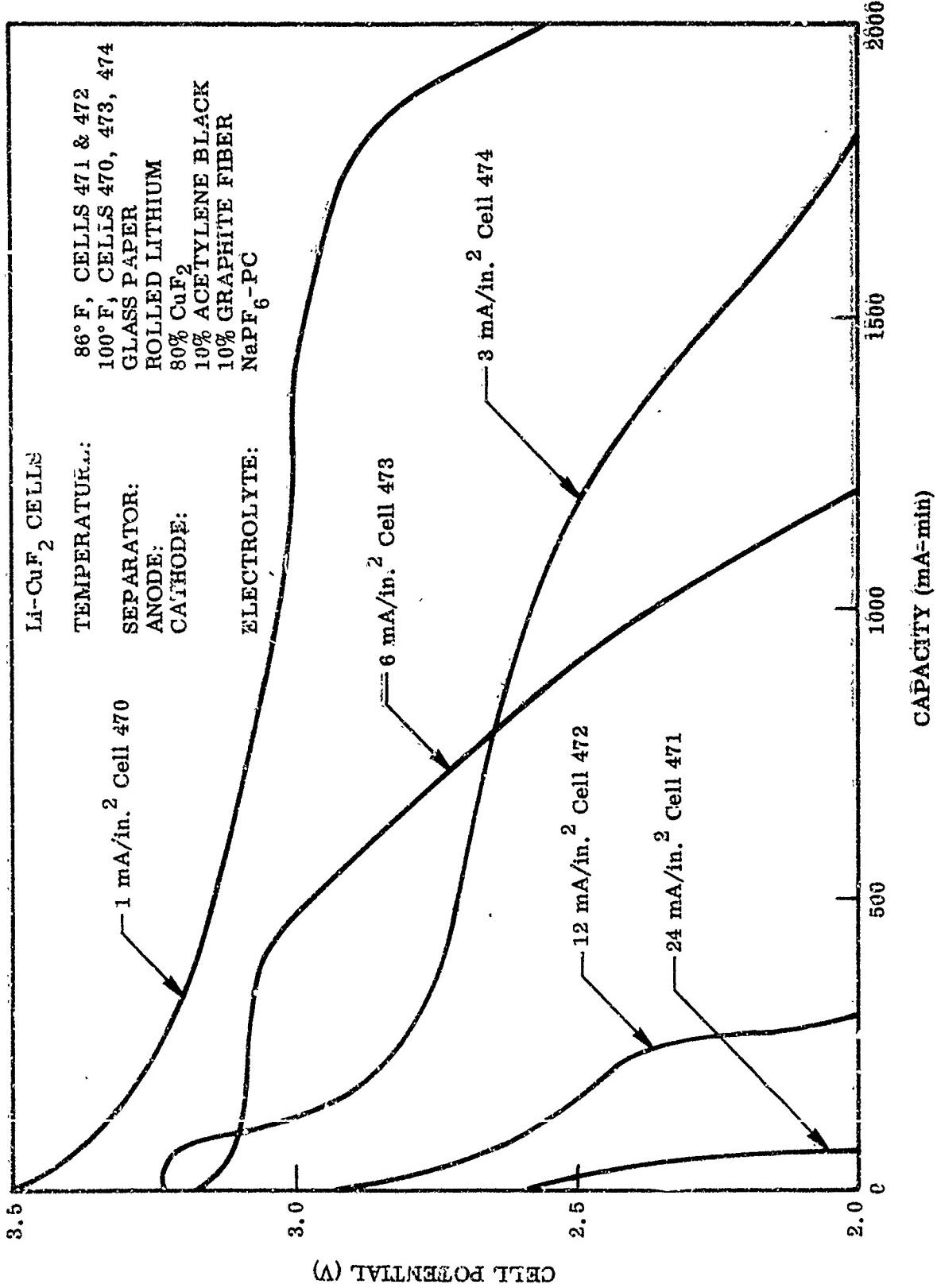


Figure 23 Discharge of Cells With Filter Cake Cathodes and Sodium Hexafluorophosphate - Propylene Carbamate Electrolyte

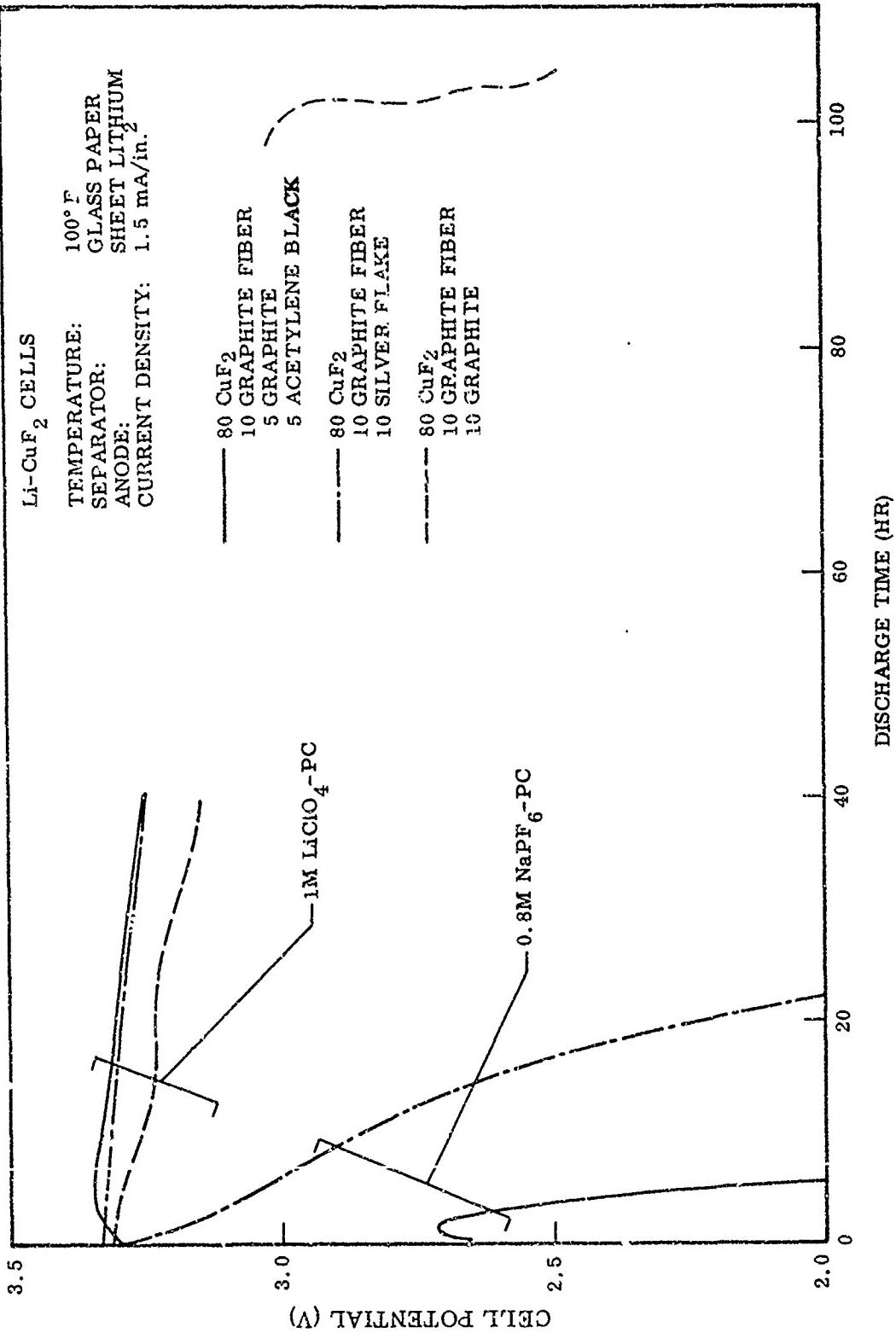


Figure 24 Comparison of Lithium-Cupric Fluoride Cells With Lithium Perchlorate and Sodium Hexafluorophosphate Electrolyte

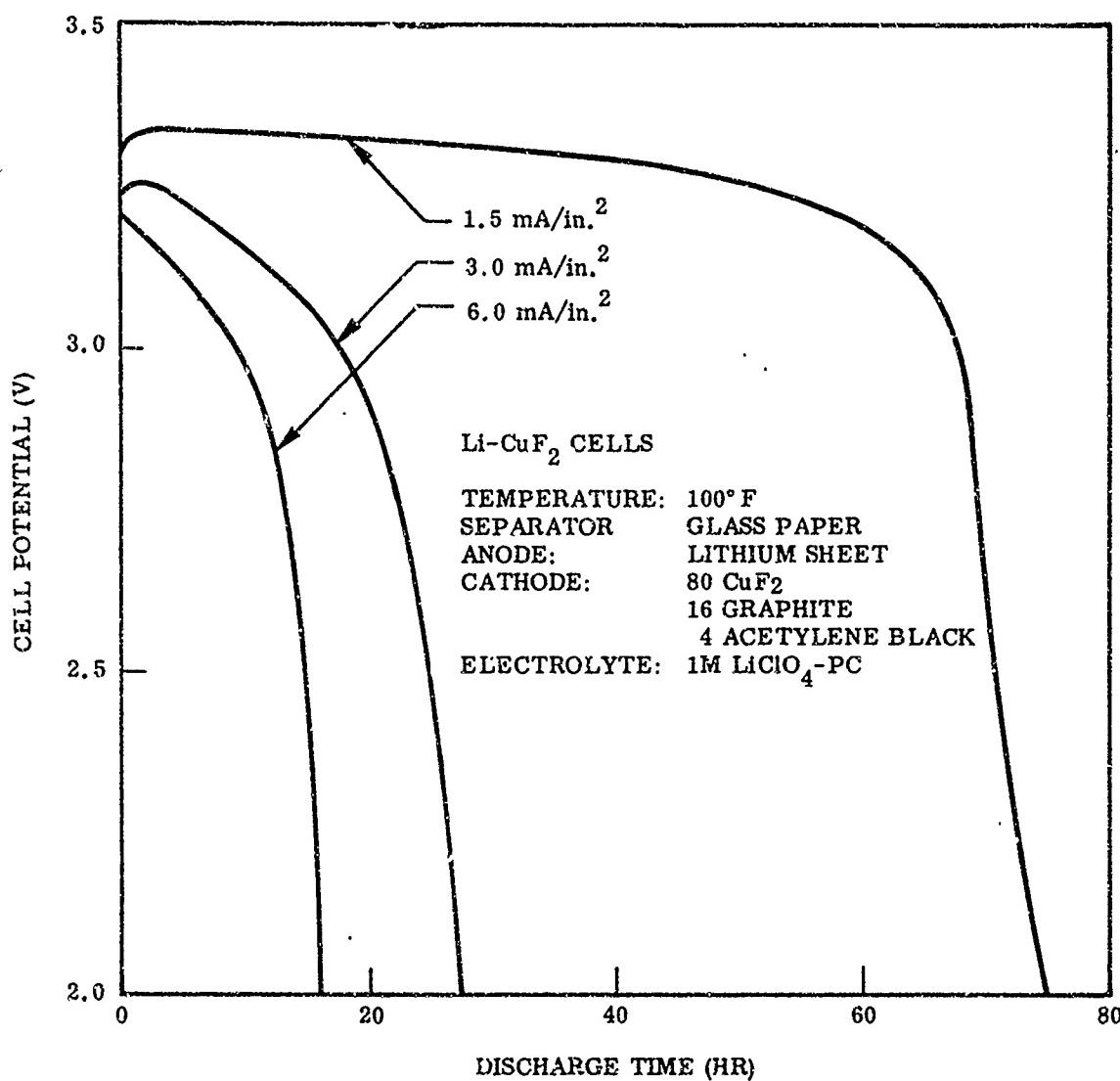


Figure 25 Discharge of Lithium-Cupric Fluoride Cells Without Graphite Fiber in the Cathode

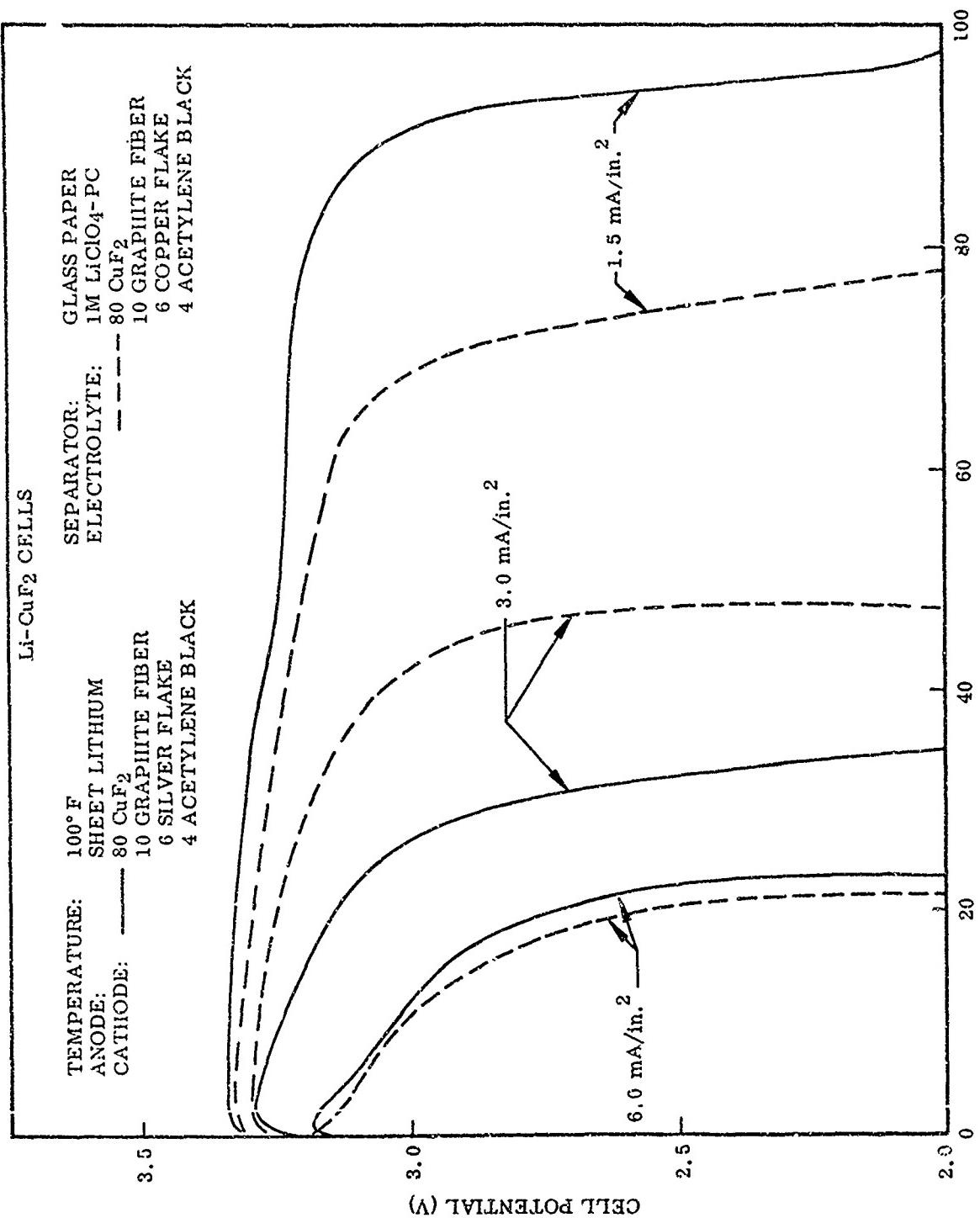


Figure 26 Discharge of Lithium-Cupric Fluoride Cells With Silver or Copper Flake in the Cathode

2.6 CALORIMETRIC INVESTIGATION OF ELECTROCHEMICAL CELL CHARACTERISTICS

The amount of heat developed by a cell during electrochemical operation is of interest (1) in cell design for fabrication of electrodes and separators in a cell structure so that efficient conduction of heat may be planned and a given cell operating temperature can be obtained; (2) as a measure of the efficiency of cell reaction, since polarization and internal resistance liberate heat during cell charge and discharge; and (3) in determination of the change in heat of reaction as a possible means for elucidation of the electrochemical cell reaction.

To gain further insight into the reactions occurring in the lithium-copper fluoride cell, the reactions were studied using a single cell measuring the voltage and heat evolution during discharge and charge operations. The lithium electrode was fabricated from lithium sheet 15 mils thick rolled onto expanded metal screen. The copper fluoride electrode was fabricated by pasting an 80% copper fluoride, 20% copper flake mixture wet with propylene carbonate electrolyte on an expanded copper screen. The electrodes were assembled with glass-fiber filter paper separators and sealed, with propylene carbonate - 0.7-mole sodium hexafluorophosphate electrolyte in polyethylene-Mylar-aluminum foil laminated bags. In the first three runs, six cells were placed in parallel, each with two lithium and one copper fluoride electrode. For the next three runs, two of the cells were removed and a group of four cells was connected in parallel. The cell and resistance heater were immersed in oil contained in a double glass Dewar. The Dewars were positioned in a constant-temperature oil bath and the Dewar contents stirred by a glass paddle driven by a synchronous motor. Visual temperature readings were made with an NBS certified mercury column thermometer. The electrical equipment used with the calorimeter is depicted in Figure 27. During a run, the temperature change determined by the recorder was measured for a given cell charge or discharge at constant current operation. The temperature change was next determined for a calibrated energy input through the resistive heater. The energy change in the cell was thus obtained by proportion as follows:

$$W_{\text{cell}} = \left(\frac{\Delta T_{\text{cell}}}{\Delta T_{\text{calibration}}} \right) W_{\text{calibration}}$$

where W is the energy in watt-seconds. The method of obtaining the temperature change compensates for the heat of stirring. Simultaneous recording of the cell voltage during the run was used to compute the average cell voltage V during the run. The change in heat of reaction ΔH is computed from these two observations for discharge by

$$\Delta H_d = \frac{nF}{jIt} W_{\text{cell}} - \frac{nF}{j} V_d$$

and for charge by

$$\Delta H_c = - \frac{nF}{jIt} W_{\text{cell}} + \frac{nF}{j} V_c$$

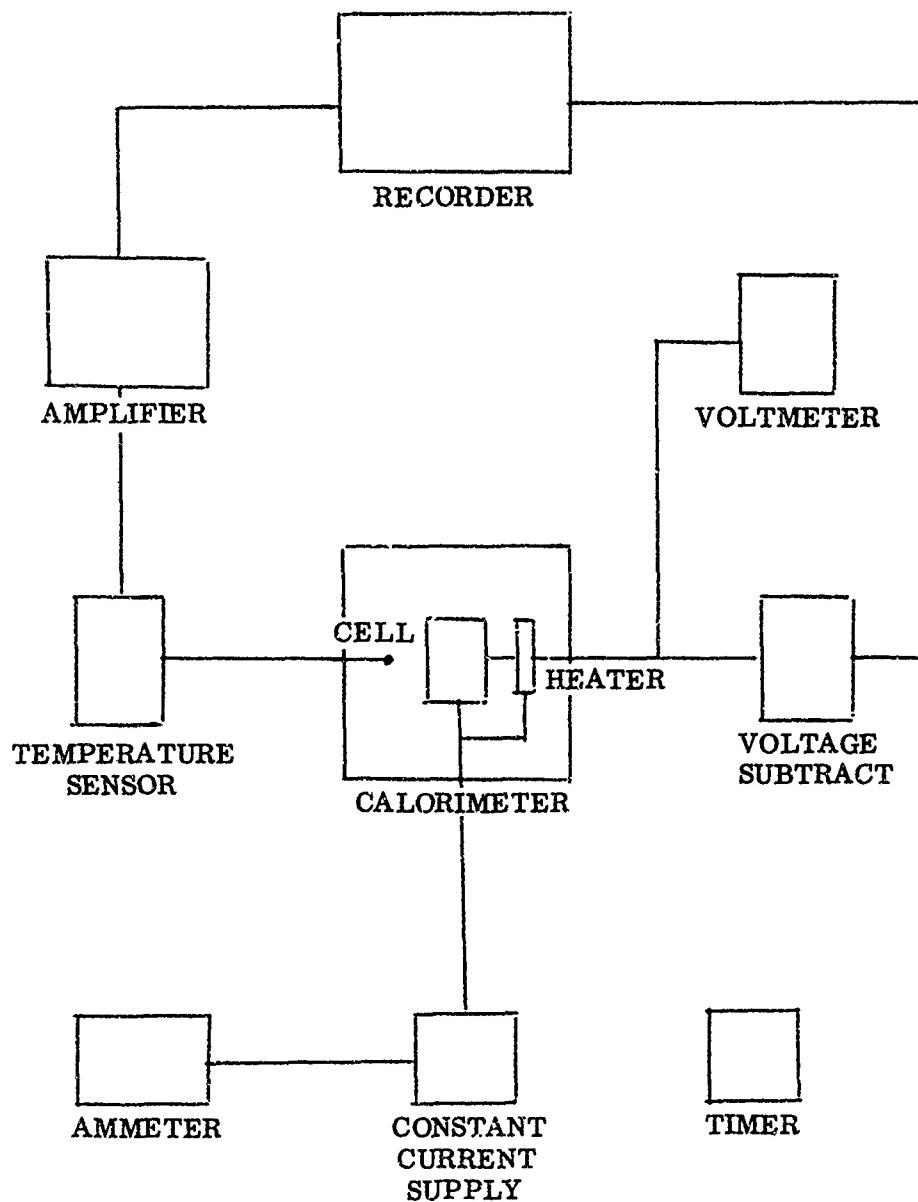


Figure 27 Block Diagram of Calorimeter Equipment

where W cell is (+) for heat evolution; i is constant current in amperes; T is time of cell run in seconds; F is the Faraday 96,500 amp-sec/equivalent; j is 4.18×10^3 kcal/mole; and n is equivalents per mole of reaction as written. The value of ΔH calculated for several experimental runs is given in Table XVII. The current densities were 0.5 mA/in.² for run 1, 0.83 mA/in.² for runs 4 through 6. On run 1, the sensitivity of the amplifier was 1,000 to 1 and together with the low current used resulted in low accuracy for the temperature change measurement. For all other runs, a sensitivity of 3,330 to 1 was used for the amplifier and a higher current was used for cell operation. On run 3, the cell pack was removed and the cell forced to occupy a smaller volume by bending electrodes, which resulted in the shorting of at least one of the cells. Since the heat developed by shorting is not accounted for by the method of heat measurement used, the value for the heat of reaction was low. The shorted cell was removed, and runs 4 through 6 were made. On run 6, a slow evolution of heat was noticed after termination of current flow and the calculated heat of reaction value was low. The values from the best runs for the heat of reaction are -73 to -77 kcal/equivalent for a reaction with one electron change (n=1). The best value for the heat of reaction for charge is +72 kcal/equivalent. It can be noted that in the absence of other chemical reactions, equal values for the heat of reaction for charge and discharge mean that the reaction is macroscopically reversible. This fact can be also demonstrated by material balance for both charge and discharge reactions. Reversibility in this cell system can be obtained only if sufficient fluoride ions are available for reaction with copper during charge.

Table XVII

CALORIMETRIC STUDY OF LITHIUM -- CUPRIC FLUORIDE CELL

Run	Mode	Current (mA)	Area (in. ²)	Open-Circuit Voltage	Average Voltage	n = 1	
						ΔH (a)	ΔF (a,b)
1(c)	Discharge	24	48	3.414	2.084	-59	-79
2(d)	Discharge	40	48	3.512	2.636	-73	-81
3	Discharge	40	48	2.87	2.306	-67	-
4	Discharge	40	32	3.335	2.633	-77	-77
5	Charge	40	32	3.362	3.920	+72	-77
6	Charge	40	32	3.175	3.816	+63	-73

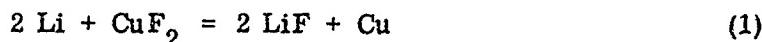
(a) kcal/equivalent.

(b) Calculated from open-circuit voltage.

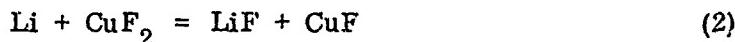
(c) Run 1, cell 396.

(d) Run 2-6, cell 411.

The theoretical values for the thermodynamic functions with solid-state components for the reaction



are for a one-electron reaction -82 kcal/equivalent for the heat of reaction and -81 kcal/equivalent for the free energy of reaction, which is equivalent to a cell voltage of 3.50 V. As an alternate reaction, the reduction of CuF_2 to CuF may be considered as



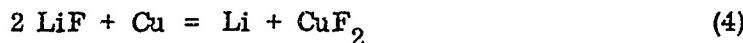
with a spontaneous but slow following reaction of



Reaction (3) is thermodynamically spontaneous, since the free energy of reaction is -4 kcal/equivalent of reaction. The heat of reaction for reaction (2) is -78 kcal/equivalent of reaction, and the free energy of reaction is -77 kcal/equivalent, which is equal to a cell voltage of 3.34 V. Although the precision of the heat of reaction measurements were within 10 %, the theoretical values differ by less than this amount.

Heat of reaction values less than -77 kcal/equivalent were found experimentally, and cell voltages near 3.3 V were noted for successive runs. It is proposed that the following reactions occur. Initially, the open-circuit voltages are 3.5 V, indicating the reaction of lithium and CuF_2 , reaction (1). When cell discharge occurs, CuF is formed and the cell voltage falls to 3.3 V, reaction (2). This change in mechanism may account for the observation in some systems of the drop and subsequent recovery of cell potential during constant current discharge. The cell voltage recovers as sufficient CuF is produced to complete the overall reaction.

The reactions which may occur on charge are the reverse of reaction (1):



for which the heat of reaction is +82 kcal/mole equivalent and the free energy of reaction +81 kcal/equivalent again corresponding to a cell voltage of 3.5 V.

An alternative charge reaction can be written as follows:



This occurs with the spontaneous following reaction



For reaction (5), the heat of reaction is +86 kcal/equivalent of reaction and the free energy change +84 kcal/equivalent, which corresponds to a cell voltage of 3.66 V. The value for the heat of reaction for charge for one determination was +72 kcal/equivalent, a value which is lower than either of the two mechanisms presented in reaction (4) or (5) which include complete cell reversibility by regeneration of the initial lithium metal and insoluble CuF₂.

If there is insufficient fluoride ion in the cell because of a low diffusion rate, then it is possible that both soluble lithium salts may be formed on discharge and soluble copper salts be formed on charge. For the reaction with ions, the following equation can be written:



Estimates of the heat of reaction changes cannot be made for propylene carbonate systems, since thermodynamic values of ions are not known. However, for aqueous ions the heat of reaction for reaction (6) is +74 kcal/equivalent. It is expected that the value for reaction (6) in propylene carbonate systems would be between 74 and 82 kcal/equivalent of reaction owing to the lower solubility of salts in propylene carbonate.

Section III

DESIGN OF 25 AMPERE-HOUR CELLS

One of the goals of this project is the assembly and discharge of 25 A-h batteries. For simplicity, a mechanical design for the cell case, terminals, and seal which had been previously developed and described in another contract report*, was utilized. In this design (Figure 28), a special polypropylene seal bushing is inserted into a hole in a commercially available aluminum can. The seal bushing is subsequently hot-formed into the shape shown in the drawing. A fluoro-elastomer O-ring is in place on the outside of the can during the hot-forming operation. An O-ring is placed on the terminal and an effective seal is made when the assembly is tightened, forcing the O-ring on the outside of the can against the can surface and the other O-ring against the chamfered edge in the seal bushing and the terminal. A polypropylene "keeper" prevents turning of the terminals when the terminal nuts are tightened, and in addition is tapped to receive a fill plug which seals with an O-ring to the can. The electrodes and separators are attached to the terminal and keeper assembly and then inserted into the can and the terminal nuts are tightened. The bottom of the can is inert gas welded in place and electrolyte added through the fill hole.

The cell design for this nominal 25 A-h cell to be discharged for 100 hr at 0.25 A uses electrodes 3.13 by 2.88 in. which have an area of 9.01 in.² per side. For a discharge rate of 1.5 mA/in.² which has been achieved with bag-type cells, 10 anodes and 9 cathodes will be needed. The projected weight for the laboratory model of the cell (Fig. 29) is given in Table XVIII.

Table XVIII

PROJECTED WEIGHT ANALYSIS OF NOMINAL 25 A-H LITHIUM-CUPRIC FLUORIDE CELL

Item	Total Weight	
	Grams	Percent
Cell Case and Hardware	122.6	28
Active Cathodic Material	101.3	23
Active Anodic Material	10.0	2
Electrode grids	67.2	15
Electrolyte	<u>140.0</u>	<u>32</u>
Total	441.1	100

With the projected discharge, this cell would deliver 75 W-hr/lb. Improvements in this figure will be obtained with increased cathode utilization, increased current density, and decreased electrolyte.

* Contract No. AF 33(615)-1195 AFAPL-TR-64-147, Lockheed Missiles & Space Company, Sunnyvale, Calif., Feb 1965.

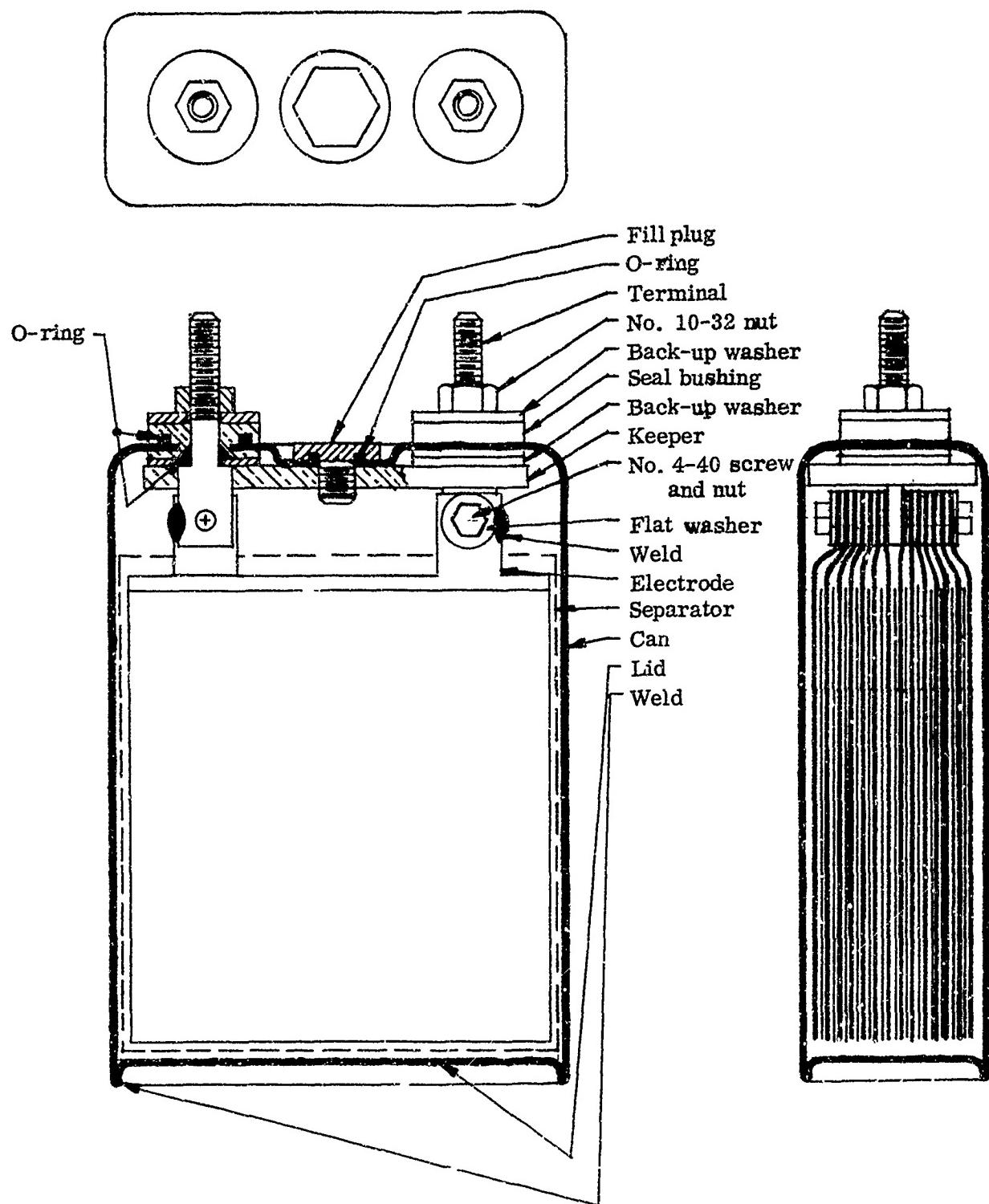


Figure 28 Mechanical Design of 25 Ampere Hour Cell

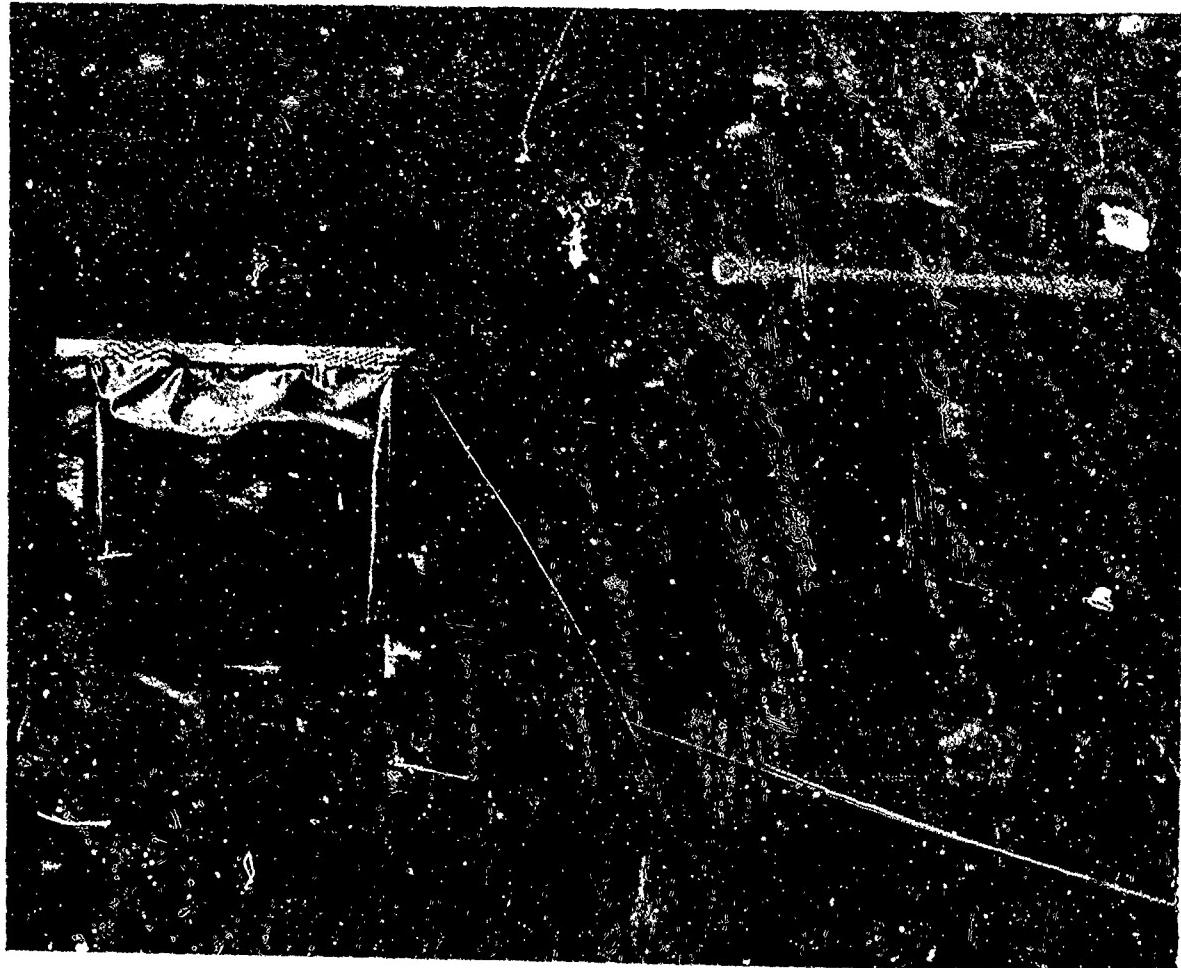


Figure 29 Plastic Bag and Aluminum Cased Twenty Five Ampere Hour Cells

Section IV CONCLUSIONS

The interest in nonaqueous solvent electrolyte systems is relatively recent and the research in this field has been limited when compared to aqueous systems. In addition, research effort has been diluted by the number of solvents, electrolyte salts, and cathodic materials that have been investigated. Lithium has received the most as an anode material. The effort of this contract has been concerned with the Li-CoF₃ and Li-CuF₂ systems and had the development of batteries with specified characteristics as a goal.

To date, work has been obtained in cell discharges and the cathode structures fabricated to date have only been capable of very low rate discharges. Probably most discouraging is the potential obtained during discharge with these cells; a single sustained voltage level is not indicated but rather a gradually declining voltage with possibly two voltage levels above 2.0 V. This poor voltage regulation not only makes the use of this couple in a battery difficult but if voltage regulation is imposed by auxiliary devices, energy to weight ratio for the system drops to values which are more readily obtained by other couples. For these reasons work with the Li-CoF₃ system will be discontinued during the remainder of this contract.

The development effort with the CuF₂ electrode has indicated that its activity is strongly influenced by the electrolyte and the supporting cathode structure. The most fruitful immediate field appears to be with the materials used in the cathode structure and the preparative method for the cathode structure to obtain high utilization of the active material and higher current densities at the cathode.

The anode polarization is minor compared to other cell losses at the present stage of development. At this time, it appears that the Li-CuF₂ system has its greatest potential during extended discharges which minimize polarization and ohmic losses in the cell. The results have shown no basic reasons to prevent the development of useful batteries from the Li-CuF₂ system and the next portion of the contract will have this goal.

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1. ORIGINATING ACTIVITY (Corporate author) Lockheed Palo Alto Research Laboratory Lockheed Missiles & Space Company Palo Alto, California		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP N/A
3. REPORT TITLE (U) Lithium-Anode Limited Cycle Battery Investigation		
4. DESCRIPTIVE NOTES (Type of report and inclusive date) Annual Report, April 1966		
5. AUTHOR(S) (Last name, first name, initial) Bauman, H. F. Chilton J. E. Mauri R. E.		
6. REPORT DATE April 1966	7a. TOTAL NO. OF PAGES 82 text pages	7b. NO. OF REFS 0
8a. CONTRACT OR GRANT NO. AF 33(615)-2455	8b. ORIGINATOR'S REPORT NUMBER(S) AFAPL-TR-66-35	
b. PROJECT NO. Task No. 817304	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) c. d.	
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13 ABSTRACT This program, to develop the technology necessary to build batteries based on the lithium-cupric fluoride and lithium-cobaltic fluoride couples, was concerned with the development of components as well as battery design. Propylene carbonate and butyrolactone were the most stable solvents studied and the majority of effort was with these solvents. Conductivities of greater than $10^{-2} \Omega^{-1} \text{cm}^{-1}$ were measured with solutions of NH_4PF_6 in propylene carbonate and several fluorine complex salts in butyrolactone. The influence of water was minimized in these and compatibility tests by direct distillation of solvent into the salt. Solutions of NaPF_6 in propylene carbonate had reasonable stability and were moderately successful as electrolyte for cell tests. Solutions of LiClO_4 in propylene carbonate gave by far the best discharges. Lithium anodes were prepared from lithium strip and dispersions and gave similar results on cell test. The selection of either type for use in batteries will depend upon fabrication simplicity. Resistance, electrolyte absorption, and retention were measured for selected separator material. Absorption was generally low for materials compatible with these cell systems. Sustained cell discharges with a voltage plateau were not obtained with $\text{Li}-\text{CoF}_3$ cells even at current densities of 0.5 mA/in.^2 . There was evidence that the cell reaction was that of the $\text{Li}-\text{CoF}_2$ couple with a reaction $2 \text{CoF}_3 + \text{Co} \rightarrow 2 \text{CoF}_2$ proceeding chemically. Discharges of 100 hr above 3.0 V were obtained with $\text{Li}-\text{CuF}_2$ cells. The best cell had 58% utilization of CuF_2 with a cell voltage above 3.0 V and delivered 60 W-hr/lb of cell weight. About one third of the cell weight was electrolyte and improved figures would be expected with larger cells where the electrolyte would be a smaller proportion of the cell weight.		

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14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Energy Storage Primary and Secondary Batteries Lithium Anodes Cabaltic Fluoride Cathodes Cupric Fluoride Cathodes Non-Aqueous Electrolytes						

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